Chemical Modification of Polysulfone Ultrafiltration Membrane Using NO$_x$ for Separation of Aqueous Ionic Solution

A thesis submitted

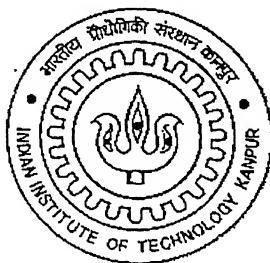*In partial fulfillment of the requirements*

For the degree of

Master of Technology

By

PRAKASH BISWAS

To the
Department of Chemical Engineering
Indian Institute of Technology Kanpur
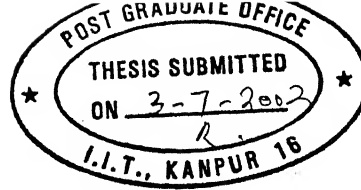### July, 2002

Dedicated to

My Grand father……

Certificate

This is to certify that the thesis entitled *"Chemical modification of Polysulfone Ultrafiltration membrane using NOx for separation of aqueous ionic solution"* done by Prakash Biswas, has been carried out under my supervision and has not been submitted elsewhere for a degree.

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Prakash Biswas

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Abstract

Commercially available polysulfone ultrafiltration membranes with 10K molecular weight cut-off (MWCO) have been modified by gas phase nitration technique using NO_x (a gas mixture of NO and NO_2). Experimental measurements have shown that the modified membranes have the exchange capacity of 4.17 m eq / dry gm of membrane and we show that this exchange capacity can be obtained only when there are about two exchangeable amine groups per repeat unit of every polysulfone molecule. A careful experimentation of the decrease in resistance suggests that hydrophilicity increase for modification. The most important variable determining the separation of ionic solution was found to be the time of ultrafiltration and its effect has been studies in the separation of monovalent (NaCl, KCl), divalent ($CaCl_2$, $MgCl_2$) and trivalent ($AlCl_3$, $FeCl_3$) salts solution. Depending upon the time of nitration we observed 0 to 4 % rejection for monovalent salts and 0 to 8 % rejection for divalent salts and 0 to 12 % rejection for trivalent salts. After amination the rejection studies shows similar order of rejection. From the data of flux versus pressure applied, hydraulic coefficient (L_p) and reflection coefficient (σ_0) were determined and they were found to be significantly different from that of the unmodified membrane. It appears that the enhanced flux of the solution could be attributed to the increased hydrophilicity of the modified membrane.

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(8 hours nitrated) Polysulfone membrane with 1000 mg / liter

aqueous $AlCl_3$ salt solution in water

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Chapter-1

Introduction: -

In order to circumvent energy intensive conventional separation schemes (distillation, extraction etc.) membrane processes (ultrafiltration, nanofiltration, reverseosmosis etc) have been adopted to perform a variety of separation operation required in different industries. The efficiencies as well as the economics of the latter can be greatly improved if the membrane processes are suitably integrated. In view of this their applications is on the rise and these processes are classified based on factor such as nature of driving force (pressure gradient, electrical gradient etc), membrane (structure, material etc), type of feed and its application (gas or liquid separation). Membrane process such as reverseosmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), dialysis, electrodialysis (ED), membrane electrolysis (ME), and diffusion dialysis (DD), are considered as first generation process; where as second generation processes are gas separation (GS), vapor permeation (VP), pervaporation (PV), membrane distillation (MD), membrane contractors (MC) and carrier mediated processes.

Nanofiltration (NF) is a relatively new membrane process used in water treatment, removal of natural organic matter (fluvic acid, humic acid etc)[1,2], salts (NaCl, Na$_2$SO$_4$, MgCl$_2$, MgSO$_4$, etc)[3,4], dyes (Reactive Black-5)[5] and organic molecules [6,7]. The process has the advantage of low operating pressure compared to reverseosmosis (RO) and a high rejection of organic molecules compared to ultrafiltration. The principle separation of removal of organic molecules and multivalent

ions from aqueous solution by nanofiltration is through a driving force, which arises due to charge interaction and size exclusion. In UF, the retention of organic species in aqueous solution can be predicted according to the nominal molecular weight cut-off (MWCO) which is an approximate size of the organic species. NF membranes are believed to be porous, with an average pore diameter of 1-2 nm and the nominal MWCO of NF membrane ranges typically from 100 to 1000.

Among the pressure driven separation process, in the RO, the solvent is adsorbed on the high-pressure side of the membrane dissolves in the membrane due to its osmotic pressure and is adsorbed from the low-pressure side of the membrane. Desalination is the main application of the reverse-osmosis and the operating pressure range is 25-135 atmosphere. In UF separation of higher molecular weight (molecular weight above 500) from aqueous and organic stream occurs by size exclusion through the microporous membrane. Ultrafiltration is an energy effective process since its operating pressure ranges is 0.5-1.0 atmosphere.

Theoretical Background: -

The rate of diffusion or flux J_i (mole cm^{-2} sec^{-1}) of molecular or ionic species across the porous plug is given by the product of three terms, namely, proportionality constant, concentration C_{ia} and force. The flux due to diffusion $J_{i(d)}$ caused by the force represented by the gradient of chemical potential $\left(-\dfrac{d\mu_i}{dx}\right)$ is given by

$$J_{i(d)} = \frac{D_i}{RT} C_i \left(-\frac{d\mu_i}{dx}\right)$$

$$= -\frac{D_i C_i}{RT}\left(\frac{d(RT \ln a_i)}{dx}\right)$$

$$= -D_i C_i\left(\frac{d \ln a_i}{dx}\right) \quad\text{————————— (1)}$$

Where D_i is the diffusion coefficient. Substituting for a_i ($a_i = C_i\gamma_i$)

$$J_{i(d)} = -D_i C_i\left(\frac{d \ln(C_i\gamma_i)}{dx}\right)$$

$$= -D_i C_i\left[\frac{d \ln C_i}{dx} + \frac{d \ln \gamma_i}{dx}\right]$$

$$= -D_i\left[C_i\frac{d \ln C_i}{dx} + C_i\frac{d \ln \gamma_i}{dx}\right]$$

$$J_{i(d)} = -D_i\left[\frac{dC_i}{dx} + C_i\frac{d \ln \gamma_i}{dx}\right] \quad\text{————————— (2)}$$

When γ_i is constant (ideal solution), the flux equation reduces to Fick's law.

$$J_{i(d)} = -D_i\frac{dC_i}{dx} \quad\text{————————— (3)}$$

The diffusion of the charged species (ions) generates an electric field (diffusion potential)

Which acts as another driving force. Thus the flux due to an electrical field $\left(-\frac{dE}{dx}\right)$ is given by

$$J_{i(e)} = -u_i z_i C_i\frac{dE}{dx} \quad\text{————————— (4)}$$

D_i is related to mobility u_i by Nernst-Einstein relation as

$$D_i = \left(\frac{RT}{F}\right)u_i$$

The total flux J_i is given by

$$J_i = J_{i(d)} + J_{i(e)}$$

$$J_i = -D_i \left[\frac{dC_i}{dx} + C_i \frac{d \ln \gamma_i}{dx} \right] - u_i z_i C_i \frac{dE}{dx}$$

$$J_i = -\frac{RT}{F} u_i \frac{dC_i}{dx} - C_i \frac{RT}{F} u_i \frac{d \ln \gamma_i}{dx} - u_i z_i C_I \frac{dE}{dx}$$

$$J_i = -\frac{RT}{F} u_i \left[\frac{dC_i}{dx} + C_i \frac{d \ln \gamma_i}{dx} + z_i \frac{F}{RT} C_i \frac{dE}{dx} \right] \hspace{1cm} (6)$$

This is the Nernst Plank Equation with activity factor included. It applies to all mobile

Species and the set of flux equations, one for each species, are subject to the condition of

electroneutrality viz. $\sum_i z_i C_i = 0$

Table-1

Recent application of membrane separation process: -

Serial No	Membrane used	System separated	Condition used	References
1.	DS-5 membrane (polysulfone polyamide)	Reactive Black-5, NaCl, water Rejection = 70 %	Temperature = 25 ^{0} C. Pressure = 0 to 30 bar. Average area = 0.029 m^2. Feed Concentration = 0.04 mol / m^3.	[7]
2.	Zirconium hydrous oxide-polyacrylate (FIP-ZPA) membrane.	Dilute solution of NaNO$_3$ – water. Rejection = 85 % At pH = 8.0	Temperature = 318 ± 1 K Pressure = 5.5 MPa. Cross flow velocity = 0.7 ± 0.05 m / sec.	[8]
3.	Desal 5DK (Desalination polyamide) prototype capillary type-2 membrane module 9891	Glucose, single salt solution (NaCl, CaCl$_2$, Na$_2$SO$_4$) and ternary ion mixtures of these salts.	a) Membrane area = 0.036 m^2. Cross flow velocity = 0.9 m / sec. Temperature = 20 ^{0} C. Pressure = 4 to 8 bar.	[9]

Serial No	Membrane used	System Separated	Condition used	References
3.	Polyether sulfone support with polyamide top layer.	Rejection NaCl ≈ 80 % $Na_2SO_4 \approx 100$ % $CaCl_2 \approx 85$ %	b) Membrane area = 0.2 m^2 Cross flow velocity = 2.7 m / sec. Temperature = 20 ^{0}C Pressure = 5 to 40 bar.	[9]
4.	Desal 5DK (Desalination polyamide) Ceramic NF membrane of γ - alumina.	NaCl, Water Rejection ≈ 80 % KCl, Water Rejection ≈ 60 %	a) Membrane area = 0.4569 m^2 $T_S = 0.0741$, $P_S = 3.319$ b) Membrane area = 0.314 m^2 $T_S = 0.531$, $P_S = 20.74$	[10]
5.	NF 20 0 Polypiperazine NF 45 Aromatic polyamide	Mixture of polyelectrolyte (sodium polyacrylate) and a monovalent salt (NaCl) Rejection ≈ 70 %	Feed concentration ratio of PE to salt is 2 to 20. Salt concentration used 1500, 15000 ppm. Recycle flow rate = 1.51 liter / minute.	[11]

Serial No.	Membrane used	System Separated	Condition used	References
6.	Aromatic polyamide thin film composite membranes.	NaCl solution. Colloidal solution (Silica particle in an aqueous suspension)	Feed concentration $= 200$ mg / lit. Temperature $= 25^{0}$ C Pressure $= 150$ psi.	[12]
7.	Poly (phthalazinone ether sulfone ketone)	PEG 12,000 PEG 20,000 and clayton yellow. Rejection $\approx 98\%$	Separation area $= 41$ cm^{2} Feed volume $= 550$ ml Pressure $= 0.1$ Mpa Temperature $= 20^{0}$ C	[13]
8.	UTC 20 MPF 44 MPF 50 MPF 60 Desal 5 Desal DK	Organic solvent Orange-2, Saframine-O, and Solvent Black 35 Rejection ≈ 54 to 100%	Membrane area $= 16.9$ cm^{2} Feed volume. $= 50$ to 30 ml Temperature $= 18$-20^{0}C Pressure $= 30$ bar.	[14]
9.	NF 45	NaCl, Na$_2$SO$_4$, MgCl$_2$. NaCl rejection $\approx 30\%$	NaCl concentration $= 4.4$ mole / m^{3} Na$_2$SO$_4$,MgCl$_2$ $= 19.4$ mole / m^{3}	[16]

Serial No.	Membrane used	System separated	Condition used	References
9.	NF 45	Na_2SO_4 Rejection $\approx 95\%$ $MgCl_2$ Rejection $\approx 90\%$	Pressure range = 30 to 1400 KPa	[16]
10.	NF 70 NF 45 UTC 20 UTC 60	Pesticides (atrazine, simazine, diuron and isoproturon). Hardness of water, Nitrates. Rejection Pesticides $\simeq 95\%$ By NF 70 Membrane. Nitrate removal $\simeq 76\%$ Hardness rejection $\approx 95\%$	Active surface area = 0.0044 m^2 Feed velocity = 0 to 7.5 meter / second Pressure = 0 to 60 bar Temperature = 25 ^{0}C.	[15]
11.	a) Desal 5 DL, Type 2540F.	CrO_4^{-2}, SO_4^{-2}, Cl^-, NO_3^-, $MgSO_4$	Membrane area = 2.5 m^2	[17]

Serial No.	Membrane used	System Separated	Condition used	References
11.	b) DOW / Filmtec NF45 Type 2540	Rejection a) $CrO_4^{-2} \approx 99\%$ $Cl^- \approx 78\%$ $MgSO_4 \approx 99$ TO 99.4 % b) $CrO_4^{-2} \approx 96.5\%$ $Cl^- \simeq 50$ to 13 %	Cross flow velocity = 1000 liter / hour. Temperature = 20 ^{0}C Pressure = 30 bar.	[17]
12.	NTR 7450 Sulfonated polyether sulfone. CA 30 (Cellulose acetate) NF 40 (Polypiperazine amide) UTC 20 (Polypiperazine amide)	NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, $LaCl_3$. Retention NaCl $\approx 78\%$ $MgSO_4 \approx 36\%$ $MgCl_2 \approx 20\%$ $Na_2SO_4 \approx 29\%$	Membrane effective area = 44 cm^2 Cross flow velocity = 6 ms^{-1} Temperature = 25 ^{0}C Pressure = 10 bar	[18]
13.	NF 70 Polyamide (Crosslinked	Methanol, Ethanol	Total effective area = 0.0044 m^2	

Serial No	Membrane used	System Separated	Condition used	References
13.	Aromatic) UTC 20 (Polyamide Zirfon polysulfone with inorganic filler)	Isopropanol, Methyl ethyl ketone, Ethyl acetate toluene, Aniline, Phenol, Cyclohexane etc.	Feed flow rate = 0 to 1000 l / b 0 to 7.5 m / sec Temperature = 25 ^{0}C Pressure = 0 to 60 bar	[19]
14.	Thin film composite membrane (TFC-S, TFC-SR, TFC-ULP) Cellulose acetate (CA-UF)	Natural Organic Matter. Surface water contained $CaCl_2$, $NaHCO_3$, NaCl. Natural organic-matter removal ⟩ 90%	Membrane area = $21.2 \times 10^{-4} \, m^2$ Pressure = 3 to 10 bar. Temperature = 20 ± 1 ^{0}C Feed solution = 185 ml	[20]
15.	PES-5, PES-10, CA 20, CA 50. PES = Polyether-sulfone CA= Cellulose-acteate.	$NaNO_3$, NaCl, Na_2SO_4, water solution. Rejection NaCl ≈ 65 % $Na_2SO_4 \approx 70$ %	Pressure = 100 to 500 KNm^{-1} Temperature = 25 ^{0}C	[21]

Serial No.	Membrane used	System Separated	Condition used	References
16.	NF 45, DK Membrane	Natural organic matter from ground water. Fe^{+2}, NO_3^-, SO_4^{-2}, Ca^{+2}, Mg^{+2}, HCO_3^- Rejection $\approx 98\%$	Operating Pressure (Max) = 1.75 MPa	[22]
17.	AFC 30 Organic tubular membrane. Polyamide on polyether sulfone. MPT 10- Polysulfone on Polypropylene. MPT 08- Polyamide on Polyethersulfone. MPT 31,34- Polysulfone on polypropylene.	Demineralize salt sea water that is separation of Na^+, K^+, Ca^{+2}, Mg^{+2}. Rejection Monovalent $\approx 50\%$ Divalent $\approx 90\%$	Effective membrane area = 0.05 m^2 / tube. Liquid recirculation system. Cross flow velocity = 1 to 3 ms^{-1}. Temperature = 25 ^0C Pressure = 10.10^5 to 40.10^5 Pa.	[23]

Objective of the present work:

As seen from the above, nanofiltration requires special membranes having pore size of the order of about 1 nm (or 10 A^0) to causes separation of ionic solution. The preparation is proprietary and sold by very selected companies. On careful observation of the analysis of ultrafiltration membranes (Nernst-Planks equation) we realized that separation is postulated to occur partially through sieving action (connective and diffusion term) and partially due to charge (electrical gradient). In view of this we decided to introduce charge on the commonly available ultrafiltration membrane and examine its effect on separation of ionic solution.

In this work we have proposed a new gas phase nitration scheme for commercial polysulfone ultrafiltration membrane using a mixture of NO and NO_2 (sometimes called NO_x). This is further aminated using hydrazine hydrate and in this process, the strength of the membrane remains unaffected. We subsequently show that the membrane material becomes charge in nature. The nitration of the membrane is substantial and in order to get the experimental exchange capacity of the modified membrane we show that every repeat unit of the polysulfone molecule must have atleast one amine group.
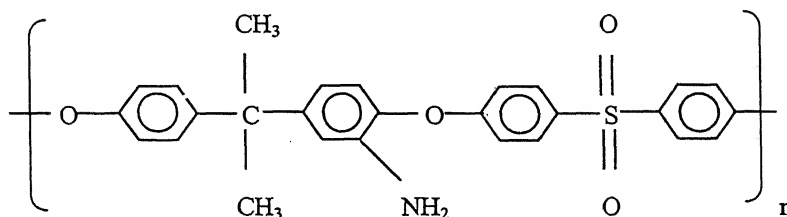
By conventional method of determination of MWCO of the membrane using nonelectrolyte molecules (e, g PEG solution in water) was found that the MWCO is reduced from 10K to 8K after modification. Further more on introduction of polar amine group shows a remarkable change in separation characteristics of electrolyte solution for example NaCl, $CaCl_2$, $AlCl_3$ solution in water, suggesting that the modified membranes is entering into nanofiltration zone.

Chapter-2

Experimental studies

2.1 Compaction of membranes: -

The membranes are washed from its preservative (glycerin, propionic acid, sodium chloride in water) by putting it in distilled water as recommended by its manufacturer (Denish Separation system) for 36 hours. The membranes are then compacted in a batch cell having the volume of 700ml. The latter is filled with a pressure gauge as shown in (fig-2.1). The compaction pressure kept is 150psi (higher than the highest operating pressure, which is 120psi) and is carried out using distilled water for 6-8 hour until constant value of flux is obtained. After the compaction is completed, the water flux is measured at seven different values of pressure to determine the hydraulic resistance (R_m) of the membrane.

2.2 Permeate flux and rejection in ultrafiltration: -

The water flux through an ultrafiltration membrane can be described by Darcy's law for flow through porous media. It states that the volumetric flux is directly proportional to the applied pressure gradient.

$$J_w = K\Delta P_{applied} = \frac{\Delta P_{applied}}{(R_m \mu_w)} \tag{1}$$

Where R_m is the intrinsic hydraulic resistance of the membrane. The rejection for a given membrane are characterized by coefficient (R_{obs} and R_{real}), which are defined as

$$\%R_{obs} = \left(1 - \frac{C_p}{C_b}\right) \times 100 \qquad (2)$$

$$\%R_{real} = \left(1 - \frac{C_p}{C_m}\right) \times 100 \qquad (3)$$

Where, C_p is the solute concentration in permeates, C_m is the solute concentration at the membrane surface and C_b is the solute concentration in bulk.

2.3 Gas phase nitration of polysulfone membranes: -

The gas phase nitration of the polysulfone membrane is done by using a three liters volume reactor as shown in fig-2.2. The reactor is made of glass and equipped with a stainless steel lid. The lid has a brass cap having an opening of 1.2mm diameter, which is sealed with silicon rubber septum. A mixture of NO and NO_2 (called NO_x) is generated in a 1.5 liter two neck flask by reacting sodium nitrite (10 gm, 0.14 gm mole) with sulfuric acid (36N, sp.gr.1.18, 25ml) in presence of ferrous sulfate (5gm, 0.072 gm mole). The flask is equipped with a rubber septum to withdraw NO_x with the help of 50ml syringe. The membrane (dry mass 0.7465gm) is placed inside the glass vessel and a small needle is introduced into the silicon rubber septum of the vessel on placing it in an oven the gas inside the bottle expands due to heating and escape through the needle. After it attains thermal equilibrium with oven kept at the desired reaction temperature, the needle is removed; the vessel is taken out of the oven and cooled to the room temperature. Approximately 500ml of NO_x gas are introduced into the reactor using the syringe for each run. When NO_x gas is introduced into the vessel, the total pressure remains about 1 atmosphere at the oven temperature and after feeding NO_x gas, the vessel

is kept back into the oven maintained at 100^0C reaction temperature. After completion of the nitration reaction, the vessel is cooled to the room temperature and the membrane is withdrawn for further modification.

2.4. Amination of nitrated Membrane: -

Amination of the nitrated membrane is carried out with hydrazine hydrate at 50^0C. The nitrated membrane is placed at the bottom of a beaker and about 100 ml of 50% hydrazine hydrate is poured over it and the beaker is made airtight by covering the mouth with aluminum foil. The membrane sample is refluxed for 4-5 hour at 50^0 C in silicon oil bath. After the reaction, the membrane is washed thoroughly with distilled water and dried in an oven at 100^0C. The membrane has now amine groups attached to the phenyl ring.
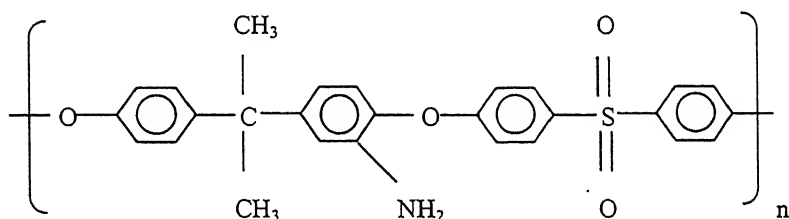
Which confirmed through FTIR spectra. This amine group can exchange chloride ions and anion exchange capacity of the aminated membrane is found out by the ASTM standard procedure.

2.5. Characterization of the Polysulfone membranes: -

The unmodified and modified polysulfone membranes are characterized with respect to the following ————

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1. Fourier Transmission Infrared Spectrum (FTIR)

2. Molecular weight cut-off (MWCO) measurement using 1% solution of Polyethylene glycol (PEG) of different molecular weight.

3. Contact angle measurements.

2.5.1. FTIR Spectra: -

FTIR Spectroscopy is one of the most useful techniques for identification of functional groups present in unmodified, nitrated and aminated polysulfone membranes are determined by Parkin Elmer 1600 FTIR spectrometer. The spectra obtained for three different cases are shown in figure (3.5)

2.5.2. Determination of molecular weight cut-off (MWCO) of the membranes: -

In general molecular weight cut-off (MWCO) is defined as the smallest molecular weight solute, which is 90% retained by the membrane. We have determined the molecular weight cut-off of the unmodified and modified polysulfone membrane by using 500ml aqueous polyethylene glycol (PEG) solution (1 wt %) of different molecular weight. The concentration of the PEG is measured by refractive index (RI) using Innco refractometer. Various molecular weight of PEG used are 200, 400, 600, 4000, 6000, 12000, 20000, and 35000. All the membranes are compacted at 150psi, and permeate is collected after 3 hour. PEG concentration in the feed, permeate and the retentate are measured.

2.5.3. Determination of Exchange capacity: -

Exchange capacity of the modified membrane is determined using the method given in ASTM standard No. ASTMD (2187, 2687, 3087, 3375 and ISI). In these procedure mixed acid first prepared and capacity determined as follows.

To prepare mixed acid, 1.8.1 ml of sulfuric acid and 27.5 ml of hydrochloride acid is added to 500 ml of water and made up to 1000 ml. Test water is prepared by adding one ml of mixed acid solution to 99 ml of water. The test water is then added to the modified membrane in a quantity of 100 ml per gm and kept for 24 hours. After this the membrane is removed and washed with distilled water till the filtrate becomes neutral. This way we are getting the membrane, which is free from mixed acid. This membrane is then mixed with 0.1N $NaNO_3$ solution, which can be prepared by mixing 8.5 gm $NaNO_3$ in 100 ml distilled water and kept for one day. Then the membrane is removed, to that solution add 1.7 gm of $AgNO_3$ with 2-3 drops of HNO_3 and the entire mass is kept 24 hours in refrigerator. The chlorine ion present in the solution from AgCl, which is precipitated. This precipitate is filtered and weighed, then the exchange capacity of modified membrane is calculated by

Exchange Capacity (meq / g) = (weight of precipitate) / (molecular weight of $AgNO_3$)

2.5.4. Contact angle measurement: -

The wetting characteristics of the unmodified, nitrated, aminated membrane are determined by measuring the contact angle with a wetting fluid. We have used distilled water as the wetting fluid. The contact angle is measured by using a Goniometer

(model 100-00-230) supplied by r'ame-heart inc. This automated equipment uses RHI 2001 image analyzing soft water measuring the dynamic contact angle. The water membrane system lives imaged using an automated camera. The field of view is illuminated with the help of a light sources. The light has to be supplied at a constant velocity. The image obtained at two different instants for a 10 hours nitrated membrane is shown in fig-2.3. A single water droplet is placed over the membrane surface by using a fine tuning microsyringe. This software measures the right side contact angle, left contact angle, height and width of the water droplet, which is in contact with the membrane. The time interval of measurement can be set according to our wish. In this work we have fixed the time interval as 1 second. This dynamic contact angle data is shown in Appendix-1. The membrane surface has to be clean without any dust particle adhering to the surface, which may give erroneous results.

2.6. Experimental setup for salt separation: -

The detailed experimental setup is shown in fig-2.1. The setup consisting of two parts, the cylindrical top part and a base plate. The entire setup is made of SS316 with a height of 240mm and an outer diameter 80mm. The cylindrical cell has a volume of 1000ml. The base plate has circular groove of 4mm depth, which houses the membrane with stainless steel support. The thin polysulfone membrane is placed on the perforated stainless steel support of 76mm diameter, then the support with the membrane is now placed inside the cylindrical groove of the base plate. The cylindrical cell is placed on the top of the casing with an O-ring between them. The O-ring thus transfers the pressure exerted by the top cell to the membrane support. The top cell is fixed to the

base plate by nut and bolt thus making the entire set a leak proof. The cell is pressurized by compressed air connected with the compressed air cylinder.

2.7. Separation experiments using monovalent, divalent and trivalent salt solution: -

The experimental set up is as described in section (2.6). All the membranes are compacted at 150psi for 6-7 hours. This is done to avoid the reduction in pore size of the membrane during the operating conditions (60-120 psi). In this work we have done the rejection studies of six different salts ($NaCl$, KCl, $CaCl_2$, $MgCl_2$, $AlCl_3$, $FeCl_3$), for each run the cell is filled with 500ml of 1000 mg/lit of different salt solution. We have studied the rejection of salts for unmodified and modified polysulfone membranes with changing the pressure as well as time of nitration. The salts concentration in feed, permeate and retentate are measured using the conductivity cell, Deluxe Conductivity meter model 601E, supplied by M.S.Electronics Pvt. Ltd. The conductivity cell is standerdized by using N/10 KCl solution. For all the experiments the cell constant is fixed at 1.444. This instruments also takes into account, the temperature dependency of the conductivity and has a resolution of 0.1 μ mho. Since we have used a batch cell the concept of steady state does not holds good. To have consistency in experiments, the permeate collected 120ml for all the runs.

ULTRAFILTRATION CELL

ULTRAFILTRATION MEMBRANE

PERMEATE COLLECTION PIPE

O-RING

BASE PLATE

LINE PRESSURE GUAGE

CYLINDER PRESSURE GUAGE

HIGH PRESSURE NITROGEN CYLINDER
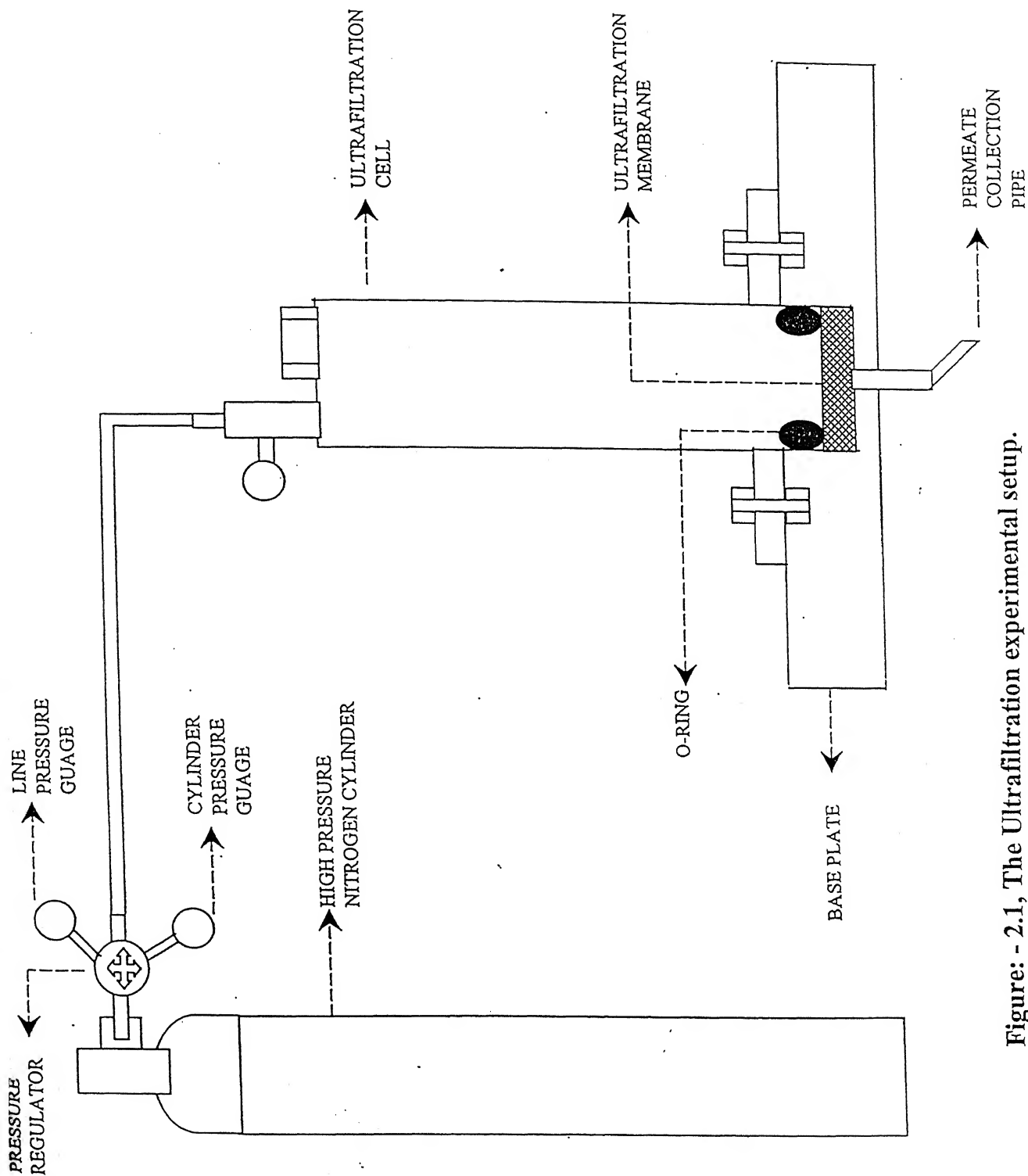
PRESSURE REGULATOR

Figure: - 2.1, The Ultrafiltration experimental setup.

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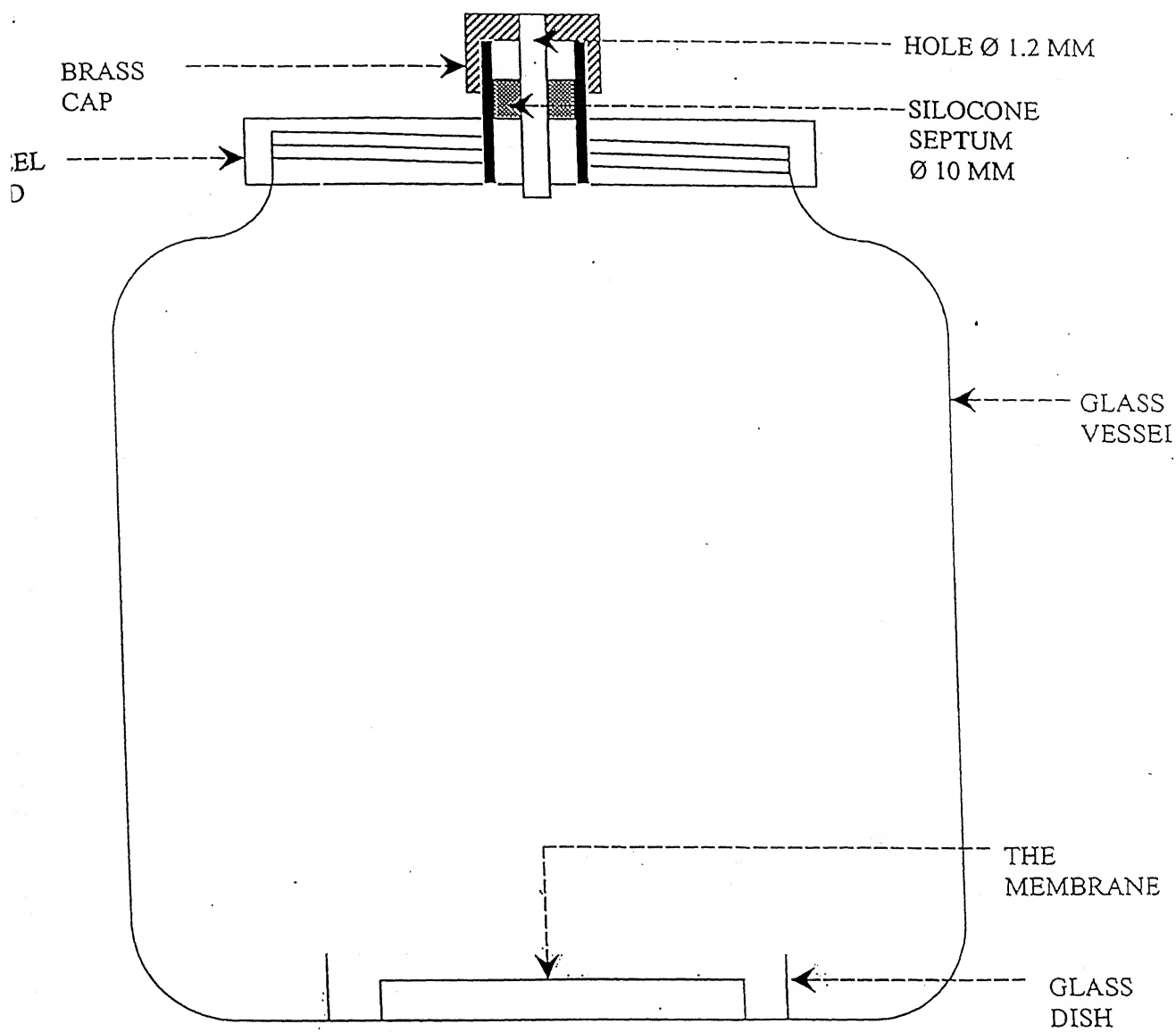
Figure: - 2.2, The nitration reactor.

22
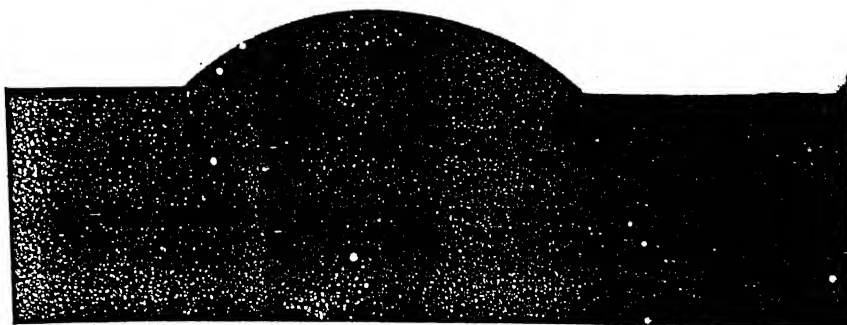
Figure: - 2.3, The image obtained by RHI 2001 software used by automated Goniometer (model 100-00-230) at two different instants for 10 hours nitrated membrane.

Chapter-3

Results and discussion: -

In this study, we have undertaken to nitrate and subsequently aminate the commercially available polysulfone membrane by reacting it with a mixture of NO and NO_2 (called NO_x gases). The mechanical strength of these modified membranes was unaffected and in the following we show that the nitration reaction is not confined to the surface alone. The effect of the extent of nitration has been examined by varying temperature and duration of the nitration reaction. These nitrated membranes are observed to have undergone a change in colour from white to light yellow and its nitrate functional groups could be reduced to amine groups by heating it with hydrazine hydrate solution. We found best result at a reaction temperature of 100 ^{0}C. However, if the temperature is increased beyond 140 ^{0}C, the membrane becomes black in colour leading to loss of its mechanical strength, making it brittle. However at a temperature around 100 ^{0}C, nitration could be sufficiently carried out. In view of this, in our study, the reaction temperature was kept at 100 ^{0} C only.

3.1. Influence of duration of nitration on rejection: -

In order to observe the influence of reaction time of nitration at 100 ^{0}C, the reaction was carried out upto 10 hours. Six reactors were placed in an oven and each reactor, containing one membrane, was withdrawn at 1hour, 2hours, 4hours, 6hours, 8hours, 10 hours. The nitrated membranes were aminated using hydrazine hydrate and now the membrane has amine functional group for exchanging. The rejection is found to

increase with the increase in time of nitration as shown in figure- (3.1.1). In this figure we have plotted the rejection vs. time of nitration of membrane for monovalent salts (NaCl, KCl), divalent salts (CaCl₂, MgCl₂), and trivalent salts (AlCl₃, FeCl₃). For unmodified membrane, for any solution, the experiment shows that the rejection is zero, which is expected. For each of these salts the solution concentration was fixed at 1000 ppm and its rejection determined through experimentation. From this figure it is seen that the rejection is the heighest for trivalent salts. As the time of nitration is increased the rejection is seen to increase from 0 to 4 % for monovalent salts, 0 to 9 % for divalent salts and 0 to 12 % for trivalent salts. For a given valencey of the salt the rejection of KCl is larger than that of NaCl, the rejection of MgCl₂ is larger than that of CaCl₂ and rejection of FeCl₃ is larger than of AlCl₃. Lastly longer duration (more than 10 hours) of nitration makes the membrane slightly brittle and has a high chance of getting torn under pressure.

At the reaction temperature, it is assumed that NO_x gives hydroxyl and hydrogen radicals (consistent with chemistry of atmosphere) as follows [26,27]

$$NO_2 \rightleftharpoons NO + \overset{\bullet}{O} \tag{1}$$

$$H_2O + \overset{\bullet}{O} \rightleftharpoons 2\overset{\bullet}{O}H \tag{2}$$

$$H_2O \rightleftharpoons \overset{\bullet}{O}H + \overset{\bullet}{H} \tag{3}$$
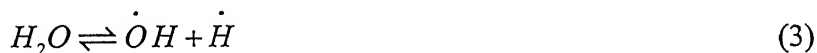
Such reaction is known to occur in atmospheric reaction giving hydroxyl radicals and in one of the recent study [28], the kinetics of formation of hydroxyl redicals have been reported in the decomposition of peroxy nitrous acid. These radicals can be formed in the gaseous medium, as well as within the polymer matrix where the small amount of

moisture is already present. The hydroxyl radicals are known to be highly reactive and can abstract hydrogen from the phenyl ring of the polymer, this way giving a radical site on it. The NO_2 molecule has a lone pair of electron, which can easily combine with this site, and overall reaction can be represented as follow.

$$\boxed{P}—C_6H_5 + \dot{O}H \rightleftharpoons \boxed{P}—C_6\dot{H}_4 + H_2O \tag{4}$$

$$\boxed{P}—C_6H_4 + NO_2 \rightleftharpoons \boxed{P}—C_6H_4 - NO_2 \tag{5}$$

$$\boxed{P}—C_6H_4 - NO_2 \xrightarrow{NH_2-NH_2, 6H_2O} \boxed{P}—C_6H_4 - NH_2 \tag{6}$$
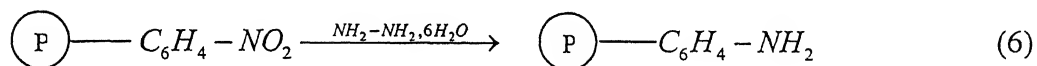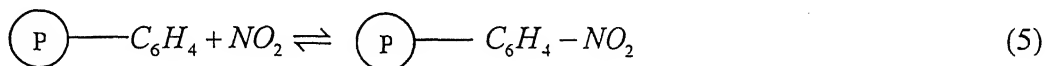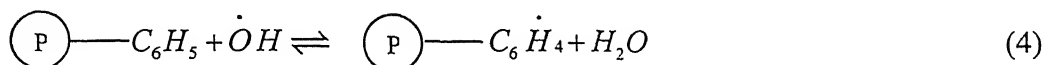
After the reduction of NO_2 group with hydrazine hydrate the membrane becomes hydrophilic in nature and this would show up by the different nature of moisture binding to the membrane.

3.2. Compaction of membrane: -

In the membrane as modified above were subjected to ultrafiltration experiments using nonelectrolyte PEG solution and the influence of the time of nitration on the flux and the rejection in batch mode were measured experimentally. The experiments in the ultrafiltration require that membrane be compacted by the procedure mentioned earlier. One of the issues that had to be settled was whether the compaction should be done before or after the nitration reaction. For this purpose, we carried out two identical experiments in which in one membrane the compaction was done before and in the other, after the modification by NO_x. The experiments showed that on compacting membranes after modification gave negligible rejection with considerably larger flux. As the modification of polysulfone membrane using NO_x has been carried out at 100 ^0C, we

suspect that the exposure to this temperature may also lead to shrinkage of pores. In view of this, we carried out blank heat treatment (without NO_x gas) of an unmodified compacted membrane for 2 and 4 hours at 100 ^{0}C to observe its effect. It has been seen that this heat treatment for both these duration increases the rejection by negligible amount and reduces the liquid flux by 8 % of 10,000 Da PEG solution. This indicates relatively small effect of the shrinkage of pores due to heat treatment at 100 ^{0}C. I n view of the above result, we compacted all the membranes before modifications were carried out.

3.3. Determination of molecular weight cut-off (MWCO) of the membranes: -

MWCO is defined as the smallest molecular mass of the nonelectrolytic macrosolute, which is 90% retained by the membrane [29]. Very dilute solution for this purpose (1 % by weight) of macrosolutes are used for determining the MWCO. The macrosolutes are globular molecules and has to be monodispersed and should be soluble in water. In this work we have used polyethylene glycol (PEG) of different molecular weight ranging from 200 to 35000. To calibrate the refractometer we have prepared different PEG solution of varying concentrations. The calibration curve is shown in figure (3.4.a). For each run, the ultrafiltration batch cell is filled with 500ml of the feed and all the membranes have been compacted beforehand at 150 psi. For determining MWCO, we have fixed the pressure at 100 psi throughout these experiments. The permeate and retentate have been collected after 3 hours and their concentrations are measured using the refractometer.

The experimental results for MWCO of the unmodified and 8 hour-nitrated membrane are shown and the cut-off curves are shown in the figure (3.3.2). The MWCO of the unmodified polysulfone membrane is observed to be 10,000 and that for 8 hour nitrated membrane has an MWCO of 8000, there is a decrease in pore size due to the nitration reaction, which appears to reduce the effective diameter of the pore.

3.4. Determination of the Exchange capacity of the modified membrane:-

The polysulfone membranes are copolymer of bisphenol-A and dichlorodiphenyl-sulfone and if it is assumed to have equimolar composition, then its one repeat unit could be represented by

$$-\left[OC_6H_4SO_2 - C_6H_4OO - C_6H_4 C(CH_3)_2 - C_6H_4\right]-$$
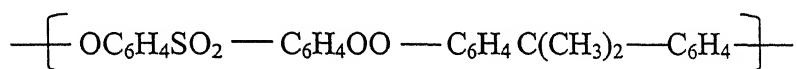
This repeat unit has a molecular weight of 446. Initially we have assumed that the polymer has one amine group per repeat unit, which contributes to the exchange capacity, and measured the exchange capacity.

After modification of the polysulfone membrane by nitration followed by amination, let us assume that the polymer has one amine group per repeat unit, which contributes to the exchange capacity. If we assume that on an average the polymer chain has N_0 repeat units per polymer molecule, meaning that it has molecular weight $446N_0$ (molecular weight of each repeat unit 446) with N_0 exchange groups on it. This polymer material would then have a theoretical exchange capacity of $N_0 / (446N_0)$ or 2.16 meq / g of dry membrane, which is independent of the molecular weight. We have observed that the 10K MWCO membrane has an average capacity 4.17 meq per dry g [30], which

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means that every repeat unit of the molecule has at least two exchange groups that contributes to the exchange capacity. This means that the nitration by NO_x gas is not confined to the surface alone but it has penetrated into the solid polymer for chemical reaction.

3.5. FTIR Analysis of the membrane: -

Figure- 3.3 shows the FTIR spectra of the unmodified, 8 hours nitrated and aminated membranes. We can clearly observe an additional peak at wavenumber 1600 cm^{-1} for $-NO_2$ group in the FTIR spectra of the nitrated membrane. No additional peak for the aminated membrane is observed.

3.6. Contact angle measurement: -

We have measured the contact angle (θ) of water for unmodified and modified membranes using automated Goniometer. Science, this instrument measures the dynamic contact angle, we have taken 600 seconds as the reference for calculating the contact angle of the membrane. The dynamic contact angle data plot is given in Appendix-1 and the data of contact angle measured after 1 and 10 minutes of study are given in table-9. From plot (3.6.1) and (3.6.2) we observe that the contact angle is decreased for both the cases from unmodified membrane to that after 10 hours nitration. The θ values is decreased from 66.09 ^{0} to 39.5 ^{0} after one minute study and from 57.5 ^{0} to 0.7 ^{0} after 10 minutes of study. The θ decreases with time of nitration mainly due to an increase in hydrophilicity.

3.7. Flux of water for modified and unmodified membranes: -

We have plotted the water flux versus pressure applied for modified and unmodified membrane in figure (3.7.1). From the figure we can clearly see a drastic increase in pure water flux of the nitrated membranes as compared to the unmodified one. The pure water flux of the modified membrane is 4 to 5 times higher than that obtained from an unmodified one and is little affected by the time of nitration. In figure-(3.7.1) the curves are observed to be linear and exactly passing through zero. From this figure the slope is determined according to equation (1) in chapter-2 and the resistance for the membrane as a function of the time of nitration is shown in figure-(3.7.2). In this figure we defined that the resistance (R_m) is exponentially decreasing. This appears to imply that in presence of NO_2 functional groups, an additional transport of water occurs due to increase in the hydrophilicity of the membrane. The exact mechanism of this increased transport is not precisely known but it appears to be because NO_2 has excess charge due to the lone pair of electrons of NO_2.

3.8. Separation experiment using aqueous solution of monovalent, divalent and trivalent salts: -

We have carried out separation experiment with 1000 mg / lit concentration of monovalent salts (NaCl, KCl), divalent salts ($CaCl_2$, $MgCl_2$), and trivalent salts ($AlCl_3$, $FeCl_3$) solution in water. The concentrations of the all salts solution have been measured by using conductivity cell (Deluxe conductivity meter model 601E, supplied by M.S

Electronics). We have determine the calibration curve for conduction vs. concentration for all the salts solution at different concentration at 25 ^{0}C and these are shown in the figure-(3.8.1) and (3.8.2). In separation experiments for each run, the cell is filled with 500ml of salt solution and the permeate flux is measured after 1.5 hours for seven different pressure because we have seen that the permeate flux becomes constant after 1.5 hours. The result obtained with unmodified and 8 hours nitrated membrane has been listed in table (10.1), (10.2) and (10.3) respectively.

We have already observed that due to nitrate and amine functional group, the membrane attains an ionic character and it is seen to facilitate separation of ionic solutes. In view of this separation of different salts (NaCl, KCl, CaCl$_2$, MgCl$_2$, AlCl$_3$, FeCl$_3$) solution (1% aqueous) was examined and the effect of the duration of the nitration on salt rejection for modified 10K-polysulfone ultrafiltration membrane was observed (figure-3.1.1). The results have been plotted in figure (3.1.1), which shows a gradual rise in rejection with duration of nitration. The modification membrane after 8 hours of nitration shows a rejection of $\approx$ 4 % for monovalent salts, $\approx$ 8 % for divalent salts and $\approx$ 12 % for trivalent salts compared to the zero percent rejection for unmodified one. This may occur from the fact that amine groups on the polysulfone backbone may interact with solvated ions, which gives higher separation. From this point of view, it appears that the modified membrane is entering into nanofiltration zone where charge effects play a role on the separation characteristics.

3.9. Solution flux for modified and unmodified membranes: -

In the figure-(3.9.1) we have plotted permeate flux for all different salts vs. applied pressure for the modified membrane. For this cases we see that the flux increases with increasing pressure and we have observed no remarkable difference in fluxes for monovalent, divalent and trivalent salts solution. After the modification of the membrane, the flux of salt solution increases nearly by a factor of two compare to that for the unmodified one.

3.10. Dependence of separation upon feed concentration: -

We have thought that by increasing the numbers of stages we would be able to enhance the separation. However the following experiment shows that this separation does not occur forever. For this purpose we have taken 250 ml of feed salts solution (1000ppm concentration) and passed through a nitrated membrane (nitrated for 8 hours) at a pressure of 100psi and allowed the solution to pass completely through the membrane. After that, the membrane is washed with water jet properly and then the 1st permeate collected is fed to the system at identical condition. The solution was allowed to pass completely and in this way we carried out the separation for 4 to 5 cycles.

Through this experiment, we have observed that for monovalent salt after 4 runs the permeate concentration becomes constant which indicates rejection of salt becomes constant. In this way we observed a maximum 6 % rejection for monovalent salt. For divalent and trivalent salt after 2 to 3 runs the permeate and retentate concentration becomes constant. On further cycles of separation, no change in rejection is observed. For divalent salts we have seen rejection ranges from 6 % to 8 % and for trivalent salts rejection varies from 11 % to 12 %.

3.11. Rejection Studies: -

In figure (3.11.1) to (3.11.2) we have plotted % salt rejection against applied pressure for all salts solution for different hour of nitrated membranes. We have seen from these plots that for all these cases, rejection increases up to pressure of 100 psi on further increases in the pressure rejection begins to fall.

Charged membranes rejects ionic solutes because of the phenomena of Donan exclusion. For a membrane containing fixed charges, the effect of Donan potential is to repel coions from the membrane and because of the electroneutrality requirement the solute itself is rejected. Solute rejection by a charged membrane depends on the charge density (related to the effective radius and valency) of the ions. In addition to this, it also depends upon the extent of interaction of fixed membrane charge sites with the ions and possible swelling (or shrinkage) of the membrane. Ions of high valency (or charge density) are rejected best [31,32]. Ions of high valency and small effective radius interact with opposite fixed charges in the membrane and may cause electrostatic cross-linking.

In figure (3.11.1), the observation may be because with increasing pressure, the charge interaction between fixed charges of the membrane and ions present in feed solution increases. As a result of this, the Donan potential effect increases which causes an increased rejection. However after a certain pressure (here 100psi) the pressure effect dominates and as a result, the solute as small as solvent molecules pass through the membrane, giving rise to lower rejection. We have also seen that rejection increases

from monovalent salts to trivalent salts, this is because according to Donan theory; ions of high valency are repulsed more strongly by the opposite charge membranes compared to these of lower valency, thus giving higher rejection.

3.12. Data analysis: -

For semipermeable membrane, the volumetric flux (J_v) across the membrane can be expressed by the well-known expression

$$J_v = L_p \left(\Delta P - \Delta \pi \right) \tag{1}$$

Where L_p is the hydraulic coefficient and P and π are the hydrostatic and osmotic pressure $\left(\pi = \Delta CRT \right)$ respectively. In most of the real system of membrane separation, the solute molecule permeates through the membrane to some extent during the process. For such membranes the flux equation is modified by introducing a correction factor σ_0, which is called osmotic reflection coefficient and equation (1) is modified to

$$J_v = L_p \left(\Delta P - \sigma_0 \Delta \pi \right) \tag{2}$$

In our studies equation (2) is valid only after $\Delta P = 30\,psi$ because this is the minimum pressure needed to cause the flow through the membrane. However for larger pressure the J_v vs. ΔP curves is essentially linear and the L_p and σ_0 can be determine by extending this line and determining the slope and intercept. In this procedure the hydraulic coefficient (L_p) is related to the slope of the line while reflection coefficient (σ_0) is related to intercept. To our purpose, we find that σ_0 values are significant and negative. This means there is a additional mechanism which enhances the flux of the solution and can be attributed to the increased hydrophilicity of the modified membrane. In figure 3.8.a and 3.8.b as a time of nitration is increases it is found that for any given

salts both these values increases and becomes asymptotic for large time of nitration. We have also observed that the value of σ_0 and L_p decreases from monovalent to trivalent salts where as for rejection fluxes studies we have seen for monovalent salts flux is more and rejection is less and for trivalent salts flux is less and rejection is more.

Chapter-4

Conclusion: -

1. In this work-studies we have studied the separation by ultrafiltration using 10K-polysulfone ultrafiltration membrane. A new gas phase nitration technique has been developed for the modification of the membrane using NO and NO_2 (called NO_x). The nitrate functional groups can be reduced to amine groups by heating it with hydrazine hydrate.

2. We have experimentally observed an exchange capacity of 4.17 m eq / gm of dry membrane and in order to get this high exchange capacity every repeat unit of the polymer should on an average have two amine groups. This implies that the modification reaction is efficient and the nitration occurs extensively.

3. Experiments showed that the membrane must be compacted before its use for the gas phase modification. In view of this, all experiments to modify the membrane were carried out after the membrane compaction was done.

4. We found that the nitration time was the most important variable, which affects the separation characteristics of the ionic solution. The hydraulic resistance of the membrane was found to decrease giving larger flux of solution with the extent of nitration indicating an increase in the hydrophilicity of the membrane.

5. The molecular weight cut off (MWCO) experiment with PEG of different molecular weight a decrease in MWCO from 10,000 to 8,000 as the time of nitration increased from 0 to 10 hours.

6. Contact angle (θ) measurements have shown that θ decreases with the time of nitration. This confirms the increase in the hydrophilic nature of the surface due to modification.

7. As the time of nitration is increased, the rejection is seen to increase from 0 to 4 % for monovalent salts 0 to 8 % for divalent salts and 0 to 12 % for trivalent salts. For a given valency of salt rejection of KCl is greater than that of NaCl and that of $MgCl_2$ is greater than that of $CaCl_2$ and $FeCl_3$ is larger than that of $AlCl_3$. After amination of the membrane there was no significant change in rejection.

8. Nitration reaction beyond 8 hours of duration showed loss of mechanical strength of the membrane. This was evident, as it could not withstand the pressure applied for ultrafiltration.

9. We have determined the hydraulic coefficient (L_p) and reflection coefficient (σ_0) as a function of time of nitration. Both these values determined are significantly different from the unmodified membrane. This means there is an additional mechanism for charge membranes, which enhances the flux of the solution and can be attributed to the increased hydrophilicity in presence of charges of the modified membrane.

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Table- 1.1

Water fluxes of polysulfone membrane at different pressure: -

Temperature $= 25^{0}C$

Membrane area $= 3.526 \times 10^{-3} m^{2}$

For Unmodified membrane		For modified membrane	
Pressure (psi)	Flux (lit / m² hour)	Pressure (psi)	Flux (lit / m² hour)
60	6.2399	60	21.6959
70	7.6821	70	22.8641
80	8.8486	80	24.6739
90	8.9251	90	27.3215
100	9.0748	100	30.6296
110	13.0465	110	35.5616
120	14.0428	120	37.8616

Table-2

Calibration data for different molecular weight polyethylene glycol (PEG) solution: -

Concentration of PEG (wt %)	Refractive index
0.00	1.33200
0.25	1.33250
0.50	1.33275
1.00	1.33367
1.50	1.33400
2.00	1.33500
3.00	1.33650
3.50	1.33700
4.00	1.33750

Table-3

Molecular Weight cut-off of the modified polysulfone membrane: -

Temperature = 30 ^{0}C

Membrane area = $3526 \times 10^{-3} m^2$

Applied pressure = 100 psi

Molecular weight of PEG	Permeate		Retentate		% Rejection
	Refractive index of permeate	Concentration of permeate (wt %)	Refractive index of Retentate	Concentration of Retentate (wt %)	
400	1.3326	1.00	1.33260	1.00	0.00
600	1.3326	1.00	1.33260	1.00	0.00
4000	1.3315	0.35	1.33225	0.90	61.11
6000	1.3322	0.15	1.33360	1.10	86.36
12000	1.3310	0.00	1.33260	1.15	100.00
20000	1.3310	0.00	1.33260	1.15	100.00

Table-4

Molecular weight cut-off of the unmodified polysulfone membrane: -

Temperature = 30 ^{0}C

Membrane area = $3.526 \times 10^{-3} m^2$

Pressure applied = 100psi

Molecular weight of PEG	Permeate		Retentate		% Rejection
	Refractive index of permeate	Concentration of permeate (wt %)	Refractive Index of Retentate	Concentration of Retentate (wt %)	
400	1.3334	1.00	1.3334	1.00	00.000
600	1.3334	1.00	1.3334	1.00	00.000
4000	1.3330	0.70	1.3335	1.25	44.000
6000	1.3324	0.30	1.3338	1.30	76.920
12000	1.3322	0.15	1.3340	1.45	89.655
20000	1.3322	0.15	1.3340	1.45	89.655

Table- 4

Calibration data for salt solution of different concentration at 25^0C

For NaCl salt solution		For KCl salt solution	
Concentration (mg / lit)	Conductivity (mmho)	Concentration (mg / lit)	Conductivity (mmho)
125	0.39	125	0.354
250	0.65	250	0.583
500	1.18	500	1.025
1000	2.10	1000	1.939

Table-6

Calibration data for salt solution of different concentration at 25^0C

For CaCl$_2$ salt solution		For MgCl$_2$ salt solution	
Concentration (mg / lit)	Conductivity (mmho)	Concentration (mg / lit)	Conductivity (mmho)
125	0.352	125	0.240
250	0.583	250	0.374
500	1.024	500	0.620
1000	1.918	1000	1.094

Table-7

Calibration data for AlCl$_3$ solution of different concentration at 25 ^{0}C.

Concentration of AlCl$_3$ (mg / liter)	Conductivity (mmho)
1000	1.403
500	0.786
250	0.428
125	0.226

Table-8

Calibration data for FeCl$_3$ solution of different concentration at 25 ^{0} C.

Concentration of FeCl$_3$ (mg / liter)	Conductivity (mmho)
1000	3.920
500	2.030
250	0.924
125	0.434

Table- 9

Variation of contact angle with the time of nitration: -

Type of membrane	Average contact angle (degree) after 1 minute Of study	Average contact angle (degree) after 10 minutes of study
Unmodified membrane	66.09	57.5
One hour nitrated membrane	57.45	24.3
Two hours nitrated membrane	49.78	17.4
Four hours nitrated membrane	48.39	16.0
Six hours nitrated membrane	48.83	13.6
Eight hours nitrated membrane	42.96	4.10
Ten hours nitrated membrane	39.50	0.70

Table- 10.1

Results of the separation experiments done with unmodified polysulfone Membrane with 1000 mg / liter aqueous NaCl solution

Applied Pressure (psi)	Pure water flux (liter / m² hour)	Permeate flux (liter / m² hour)	Permeate	
			Conductivity (mmho)	Concentration (mg / liter)
70	7.6821	9.9257	1.818	995.8732
80	8.8486	10.7765	1.923	999.3273
90	8.9251	13.8956	1.909	994.5862
100	9.0748	16.7322	1.914	998.1973
110	11.5862	18.5639	1.915	997.7259
120	13.0465	20.6835	1.913	996.4296

Applied pressure (psi)	Retentate		% Rejection $\left(1-\dfrac{C_p}{C_r}\right)\times 100$
	Conductivity (mmho)	Concentration (mg / liter)	
70	1.818	995.8732	0
80	1.923	999.3273	0
90	1.909	994.5862	0
100	1.914	998.1973	0
110	1.915	997.7259	0
120	1.913	996.4296	0

Table-10.2

Results of the separation experiments done with 8hours nitrated polysulfon membrane with 1000 mg / liter aqueous $CaCl_2$ solution.

Applied pressure (psi)	Pure water flux (liter / m² hour)	Permeate flux (liter / m² hour)	Permeate	
			Conductivity (mmho)	Concentration (mg / liter)
70	22.8641	23.2979	1.834	943.3597
80	24.6739	25.4874	1.833	943.5165
90	27.3215	28.5672	1.827	938.0243
100	30.6296	30.2974	1.798	924.3516
110	33.2953	33.5874	1.809	928.433
120	37.1764	35.4867	1.791	917.7153

Applied pressure (psi)	Retentate		% Rejection $\left(1 - \dfrac{C_p}{C_r}\right) \times 100$
	Conductivity (mmho)	Concentration (mg / liter)	
70	1.909	990.5932	4.7682
80	1.918	999.2973	5.5820
90	1.936	1002.1274	6.3967
100	1.937	1006.6251	8.1732
110	1.918	998.6329	7.0296
120	1.809	985.5963	6.8873

Table-10.3

Results of the separation experiments done with 8 hour nitrated
polysulfone membrane with 1000 mg / liter aqueous $AlCl_3$ salt solution.

Applied pressure (psi)	Pure water flux (liter / m² hour)	Permeate flux (liter / m² hour)	Permeate	
			Conductivity (mmho)	Concentration (mg / liter)
70	22.8641	21.8976	1.198	819.9691
80	24.6739	23.0287	1.264	864.5103
90	27.3215	24.5873	1.407	893.1145
100	30.6296	26.8292	1.272	878.4522
110	33.2953	28.9857	1.286	885.9959
120	37.1764	31.5673	1.293	889.9492

Applied pressure (psi)	Retentate		% Rejection $\left(1-\dfrac{C_p}{C_r}\right)\times100$
	Conductivity (mmho)	Concentration (mg / liter)	
70	1.307	899.3235	8.824
80	1.379	950.3873	9.036
90	1.435	998.5963	10.563
100	1.443	1005.009	12.5926
110	1.436	1003.302	11.692
120	1.421	1000.8651	11.082
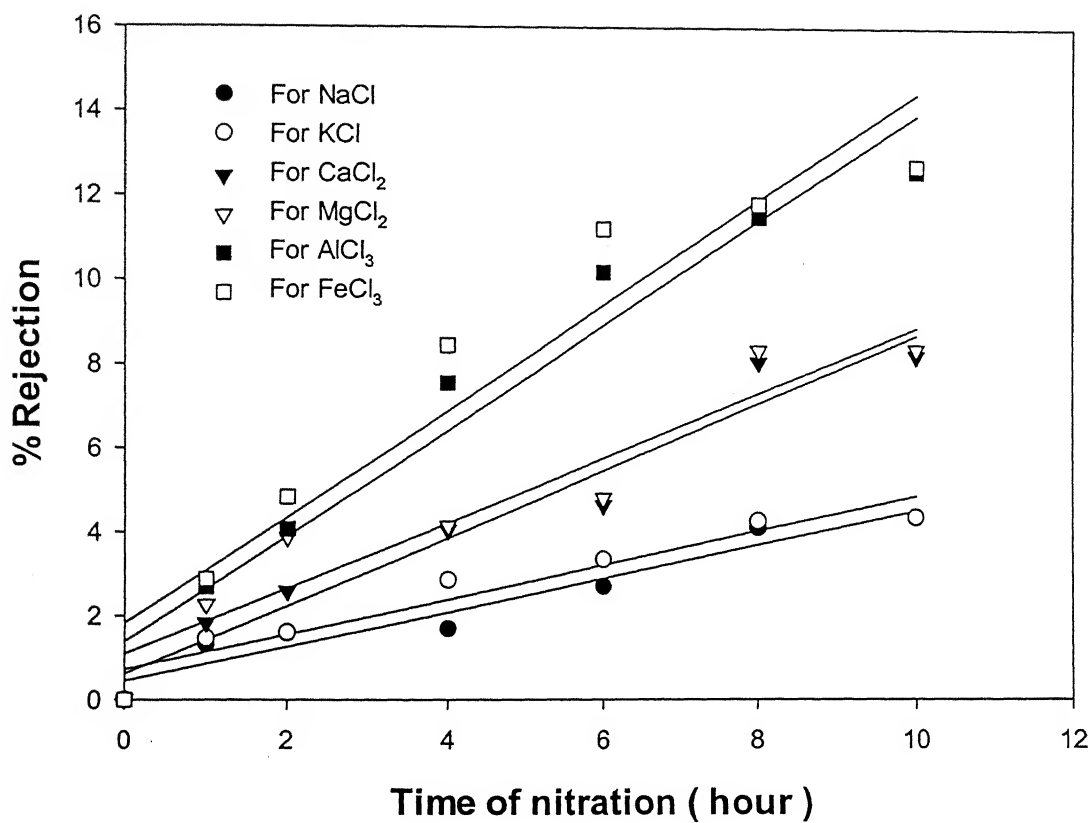
Fig:-3.1.1, Rejection vs time of nitration for different salt solutions.
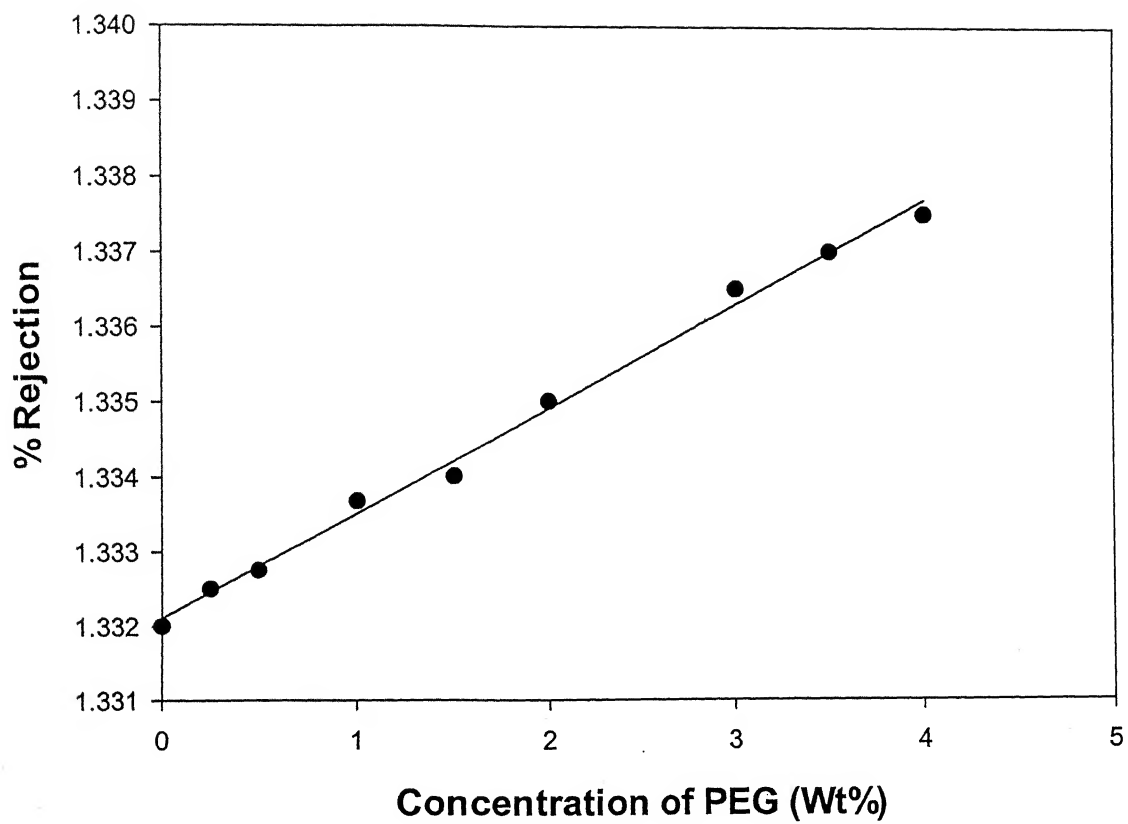
Fig:-3.3.1, Calibration curve for Polyethylene Glycol (PEG)
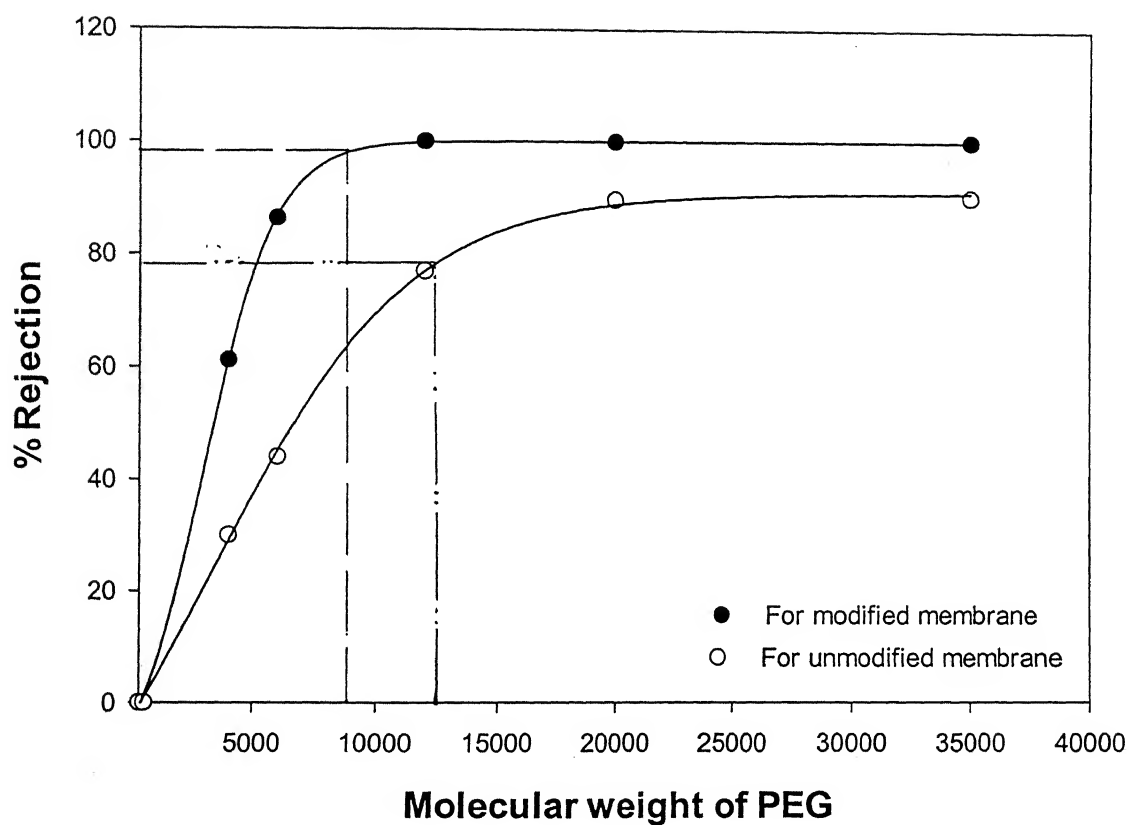
Fig:-3.3.2, Molecular weight Cut-off curves for unmodified and nitrated polysulfone membrane.
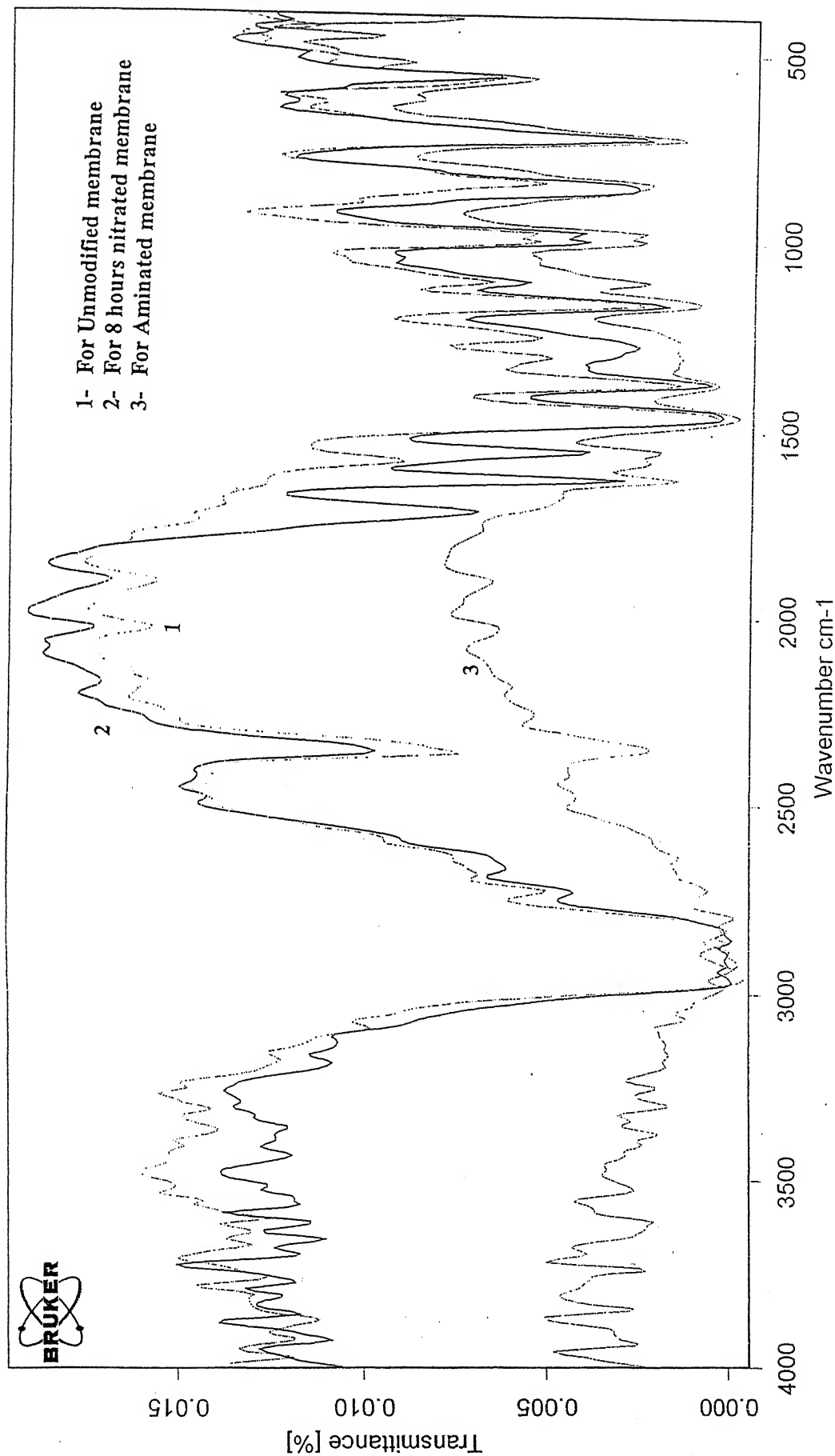
Figure: - 3.5, FTIR Spectra of the unmodified, nitrated and aminated Polysulfone membranes.
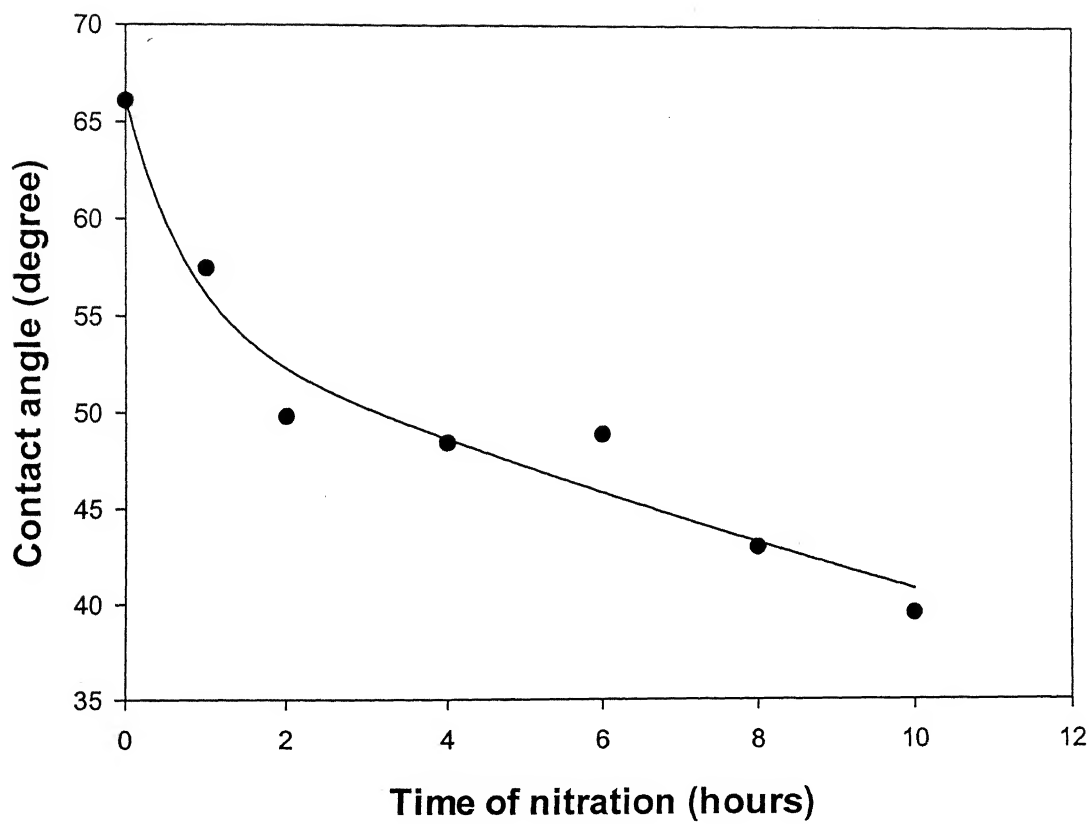
Figure :- 3.6.1, Effect of nitration on contact angle
after 1 minute of study.
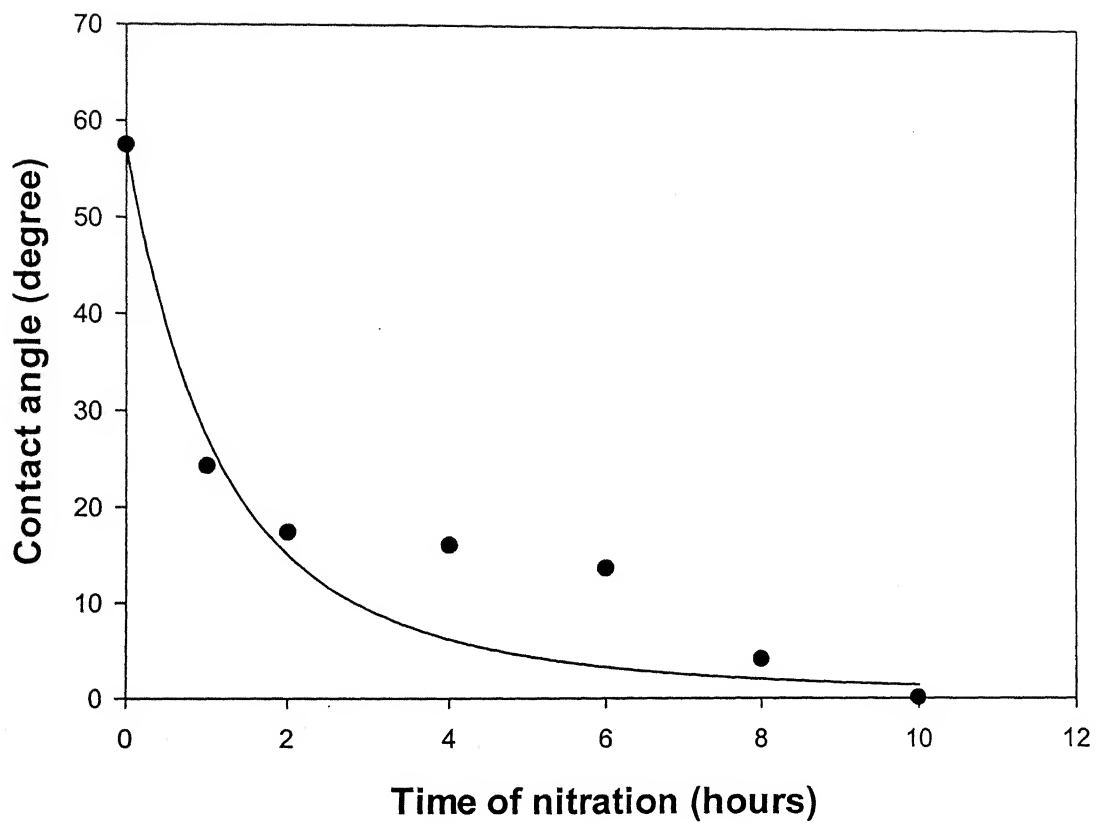
Fig:-3.6.2, Effect of nitration on contact angle
after 10 minutes of study.
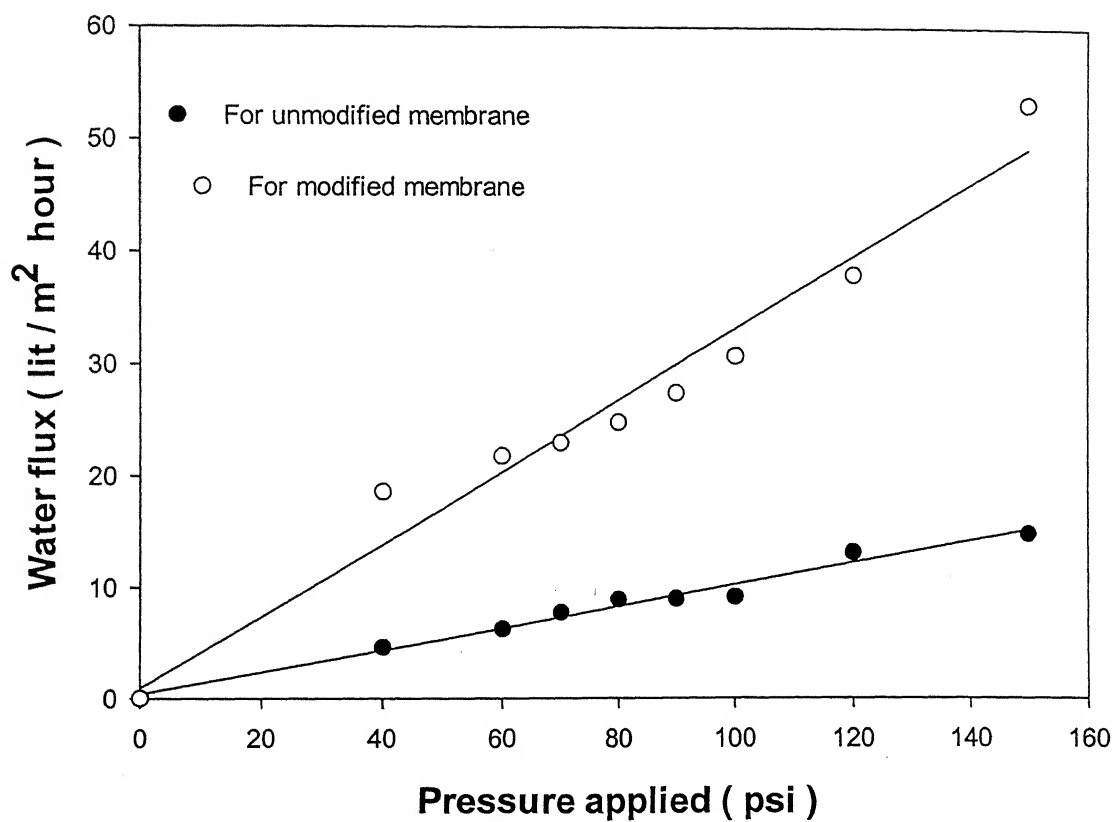
Fig:-3.7.1, Water flux vs applied pressure plots for unmodified and modified (8 hours nitrated) membranes.
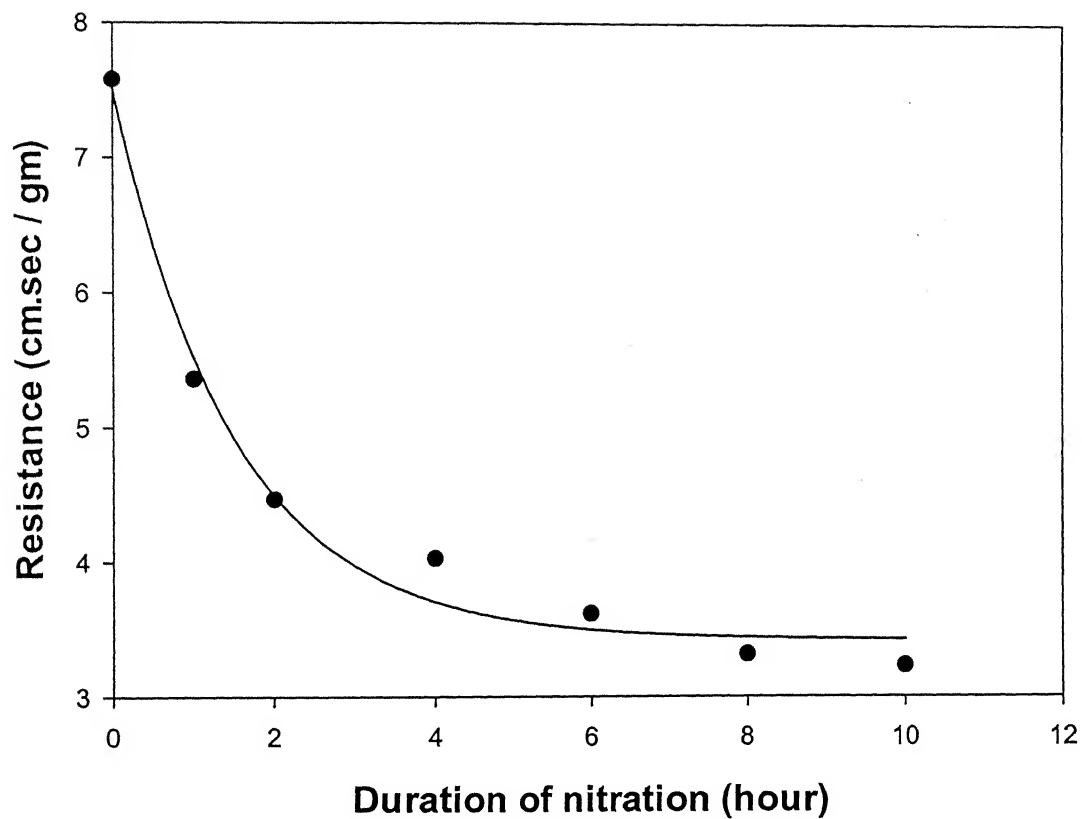
Fig:-3.7.2, Effect of duration of nitration upon membrane flow resistance of modified polysulfone membrane.
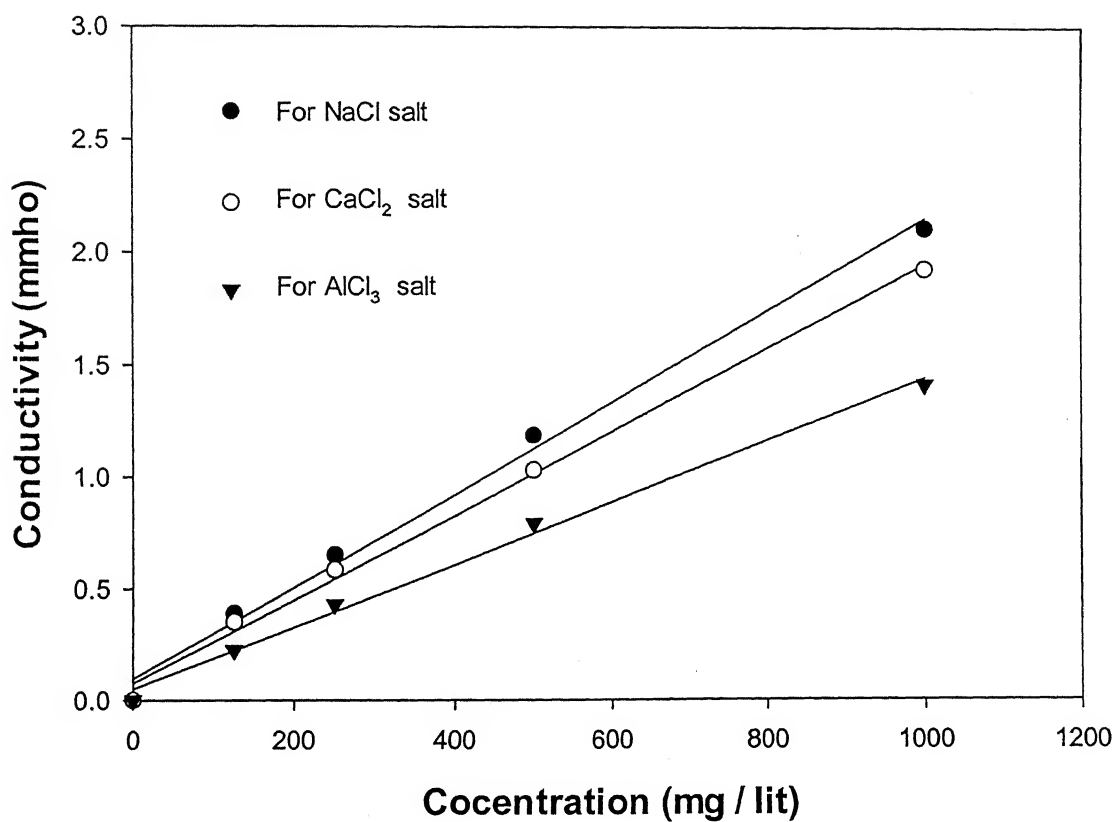
Figure-3.8.1, Calibration curves of different salts solution in water.
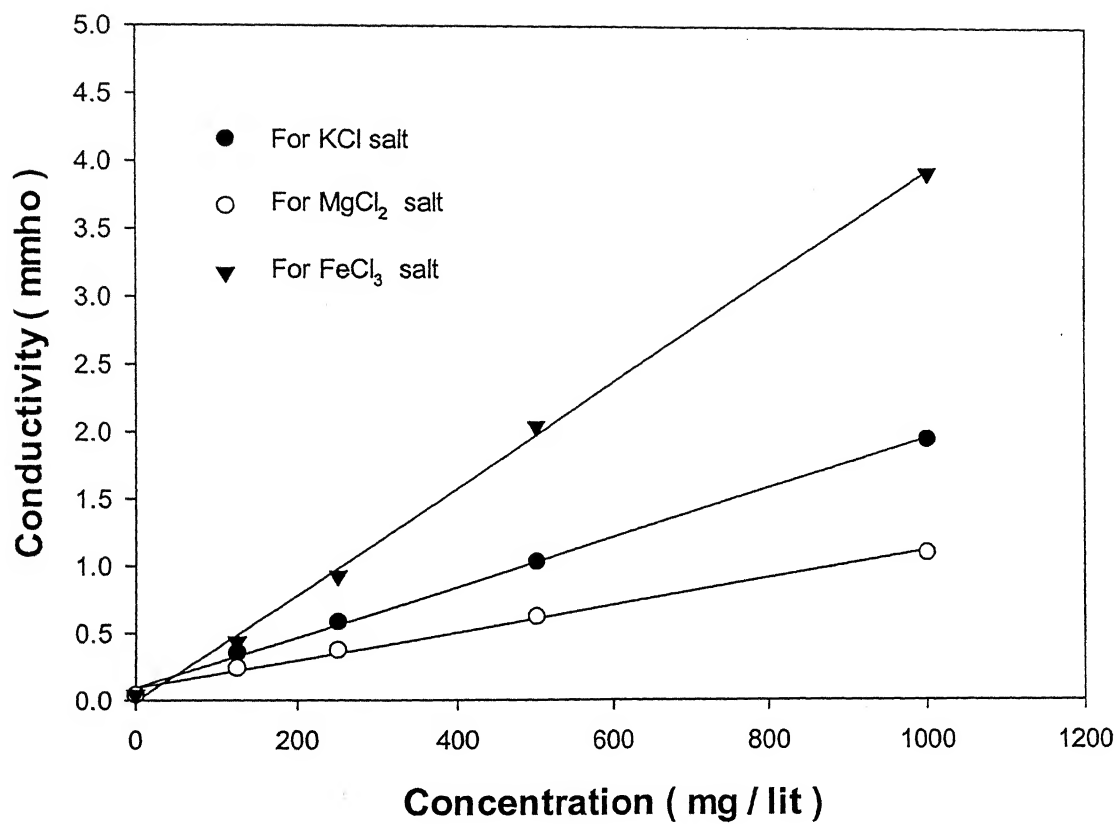
Fig:-3.8.2, Calibration curves of different salts solution in water.
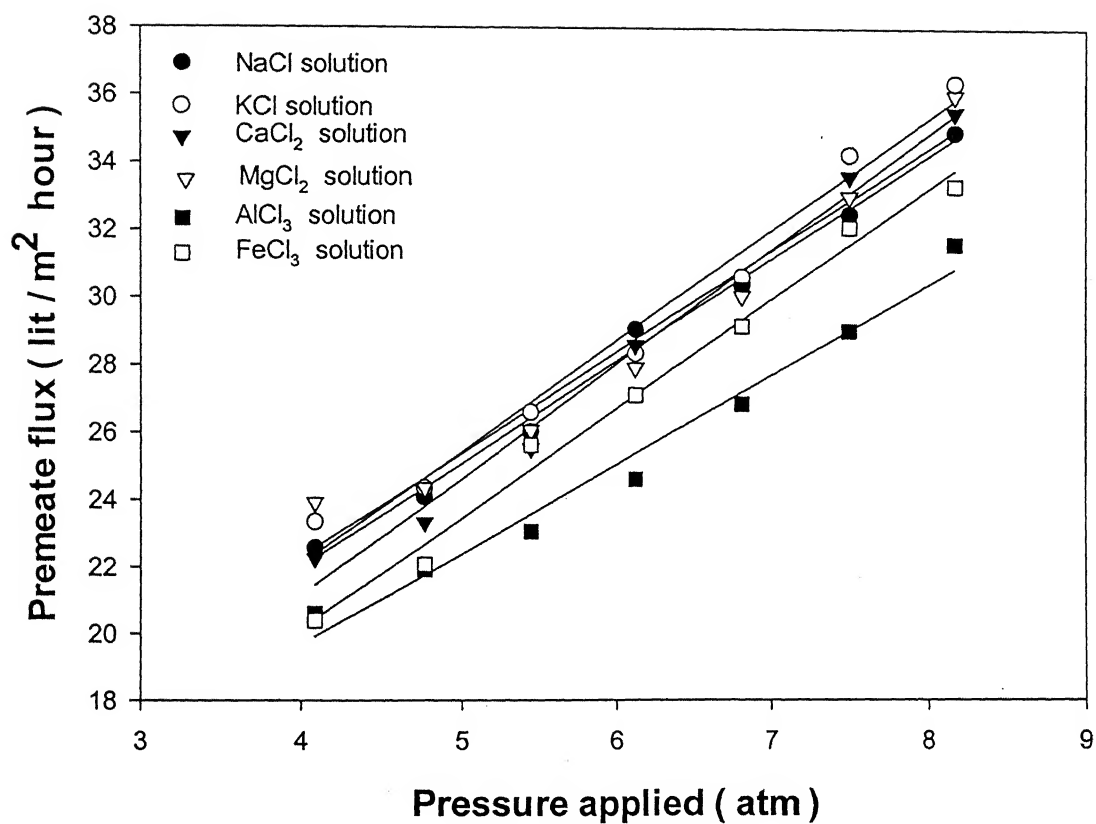
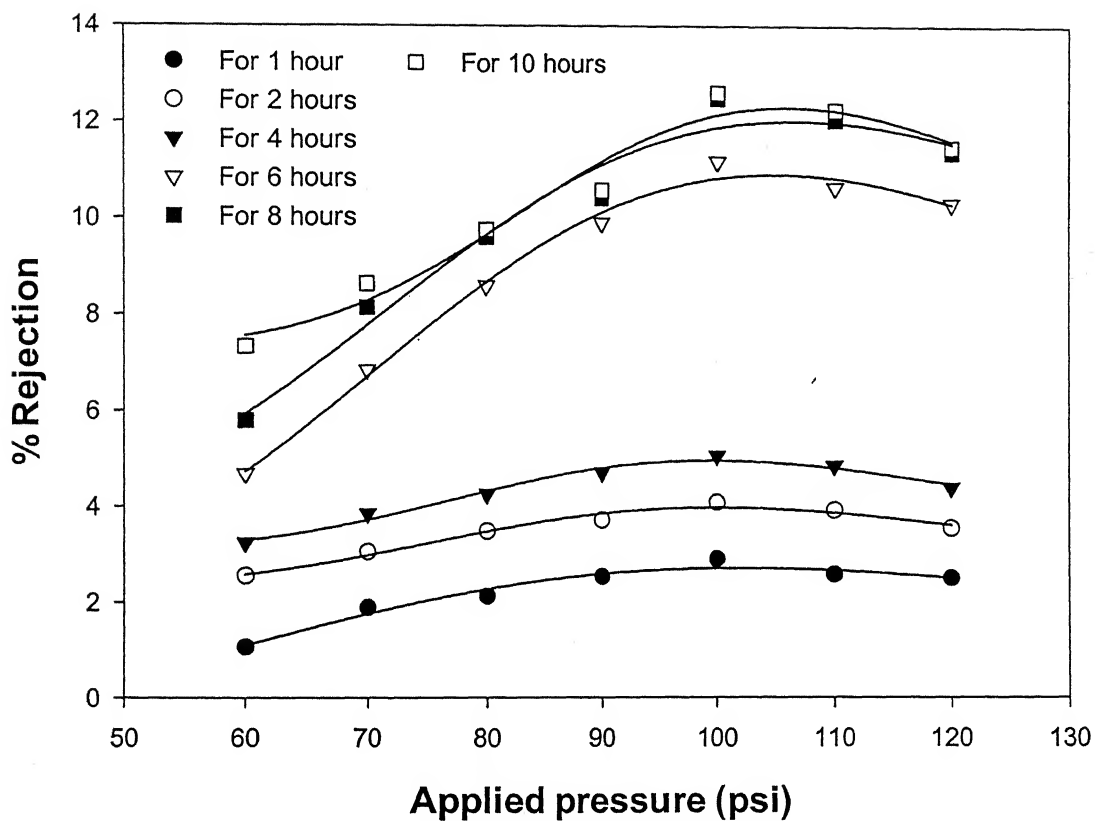Fig:-3.9.1, Flux vs Applied pressure plots for different salts for modified membranes.
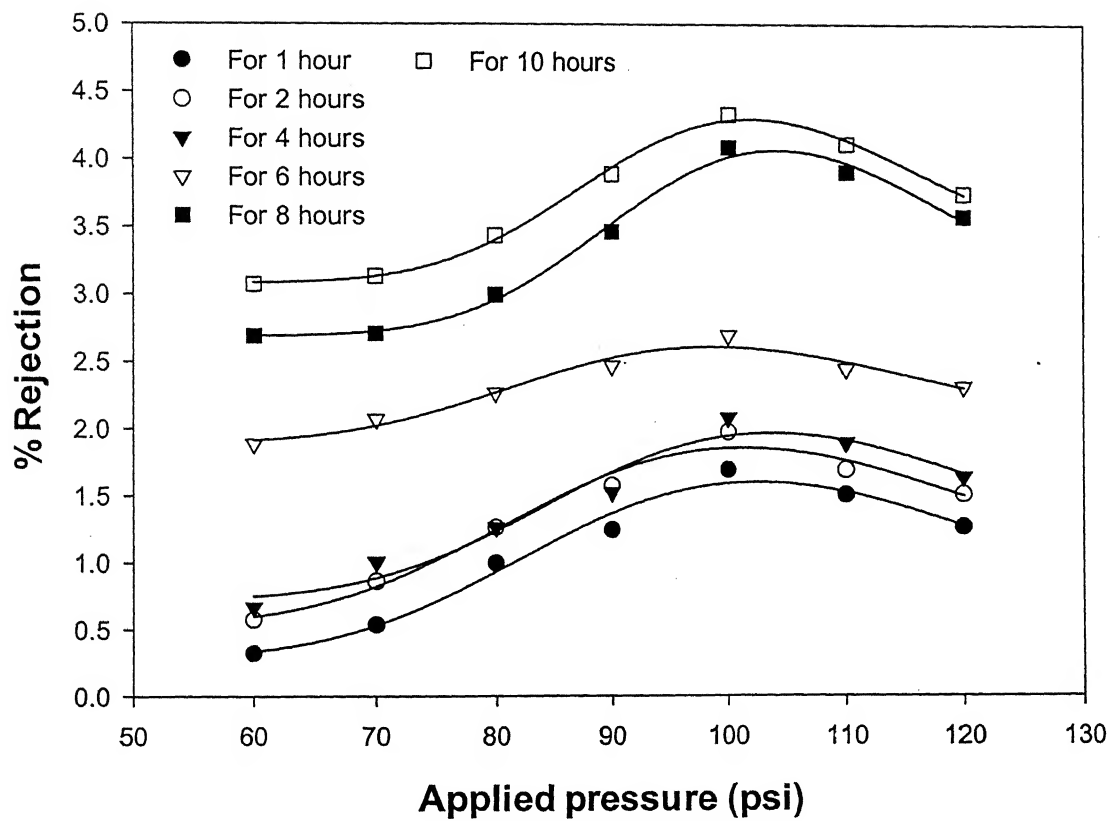
Figure-3.11.1, Rejection curves for NaCl salt solution for different hours nitrated membrane.
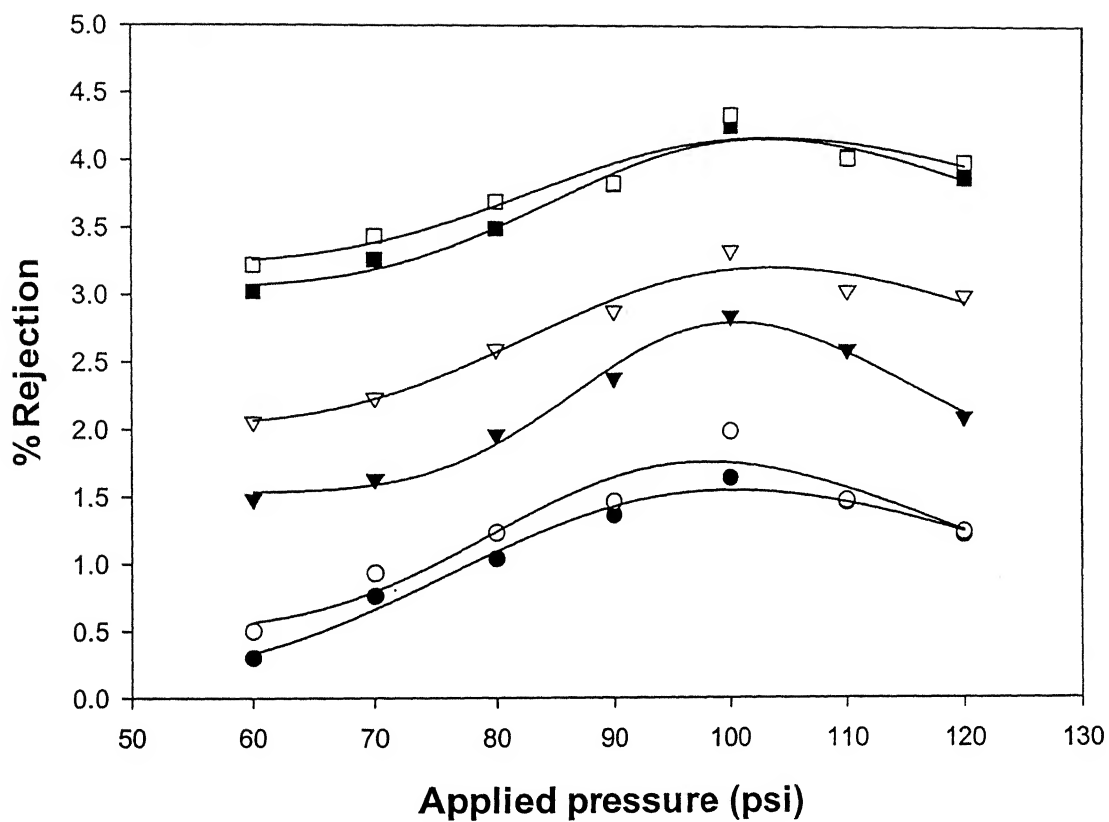
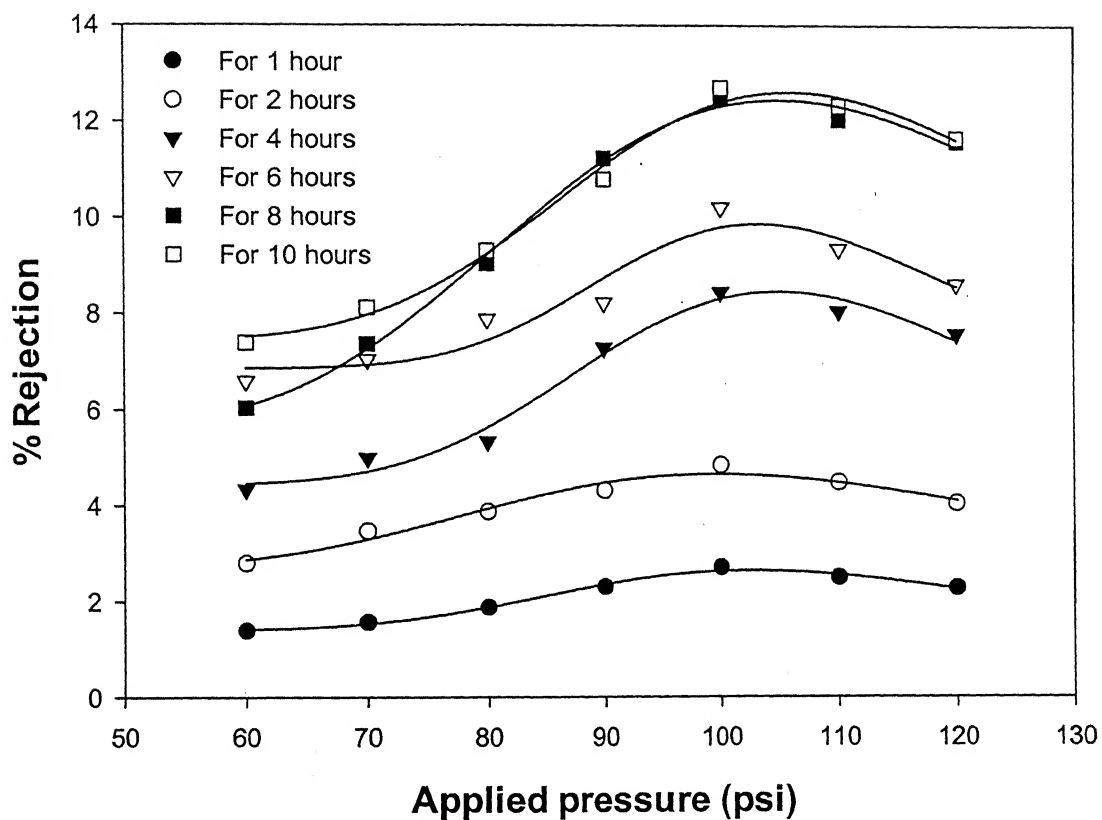Figure-3.11.2, Rejection curves for KCl salt solution for different hour nitrated membrane.

| ● | For 1hour | ○ | For 2 hours | ▼ | For 4 hours |
| ▽ | For 6 hours | ■ | For 8 hours | □ | For 10 hours |
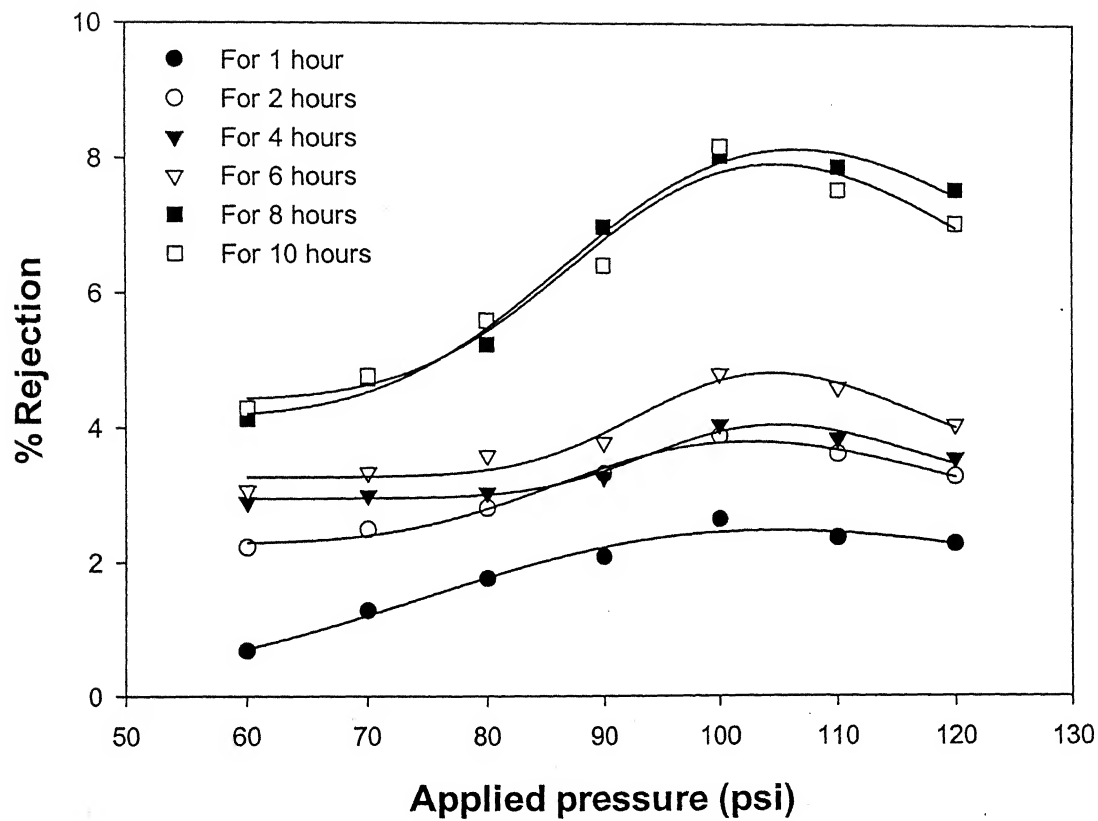
Figure-3.11.3, Rejection curves for CaCl$_2$ salt solution for different hours nitrated membranes.
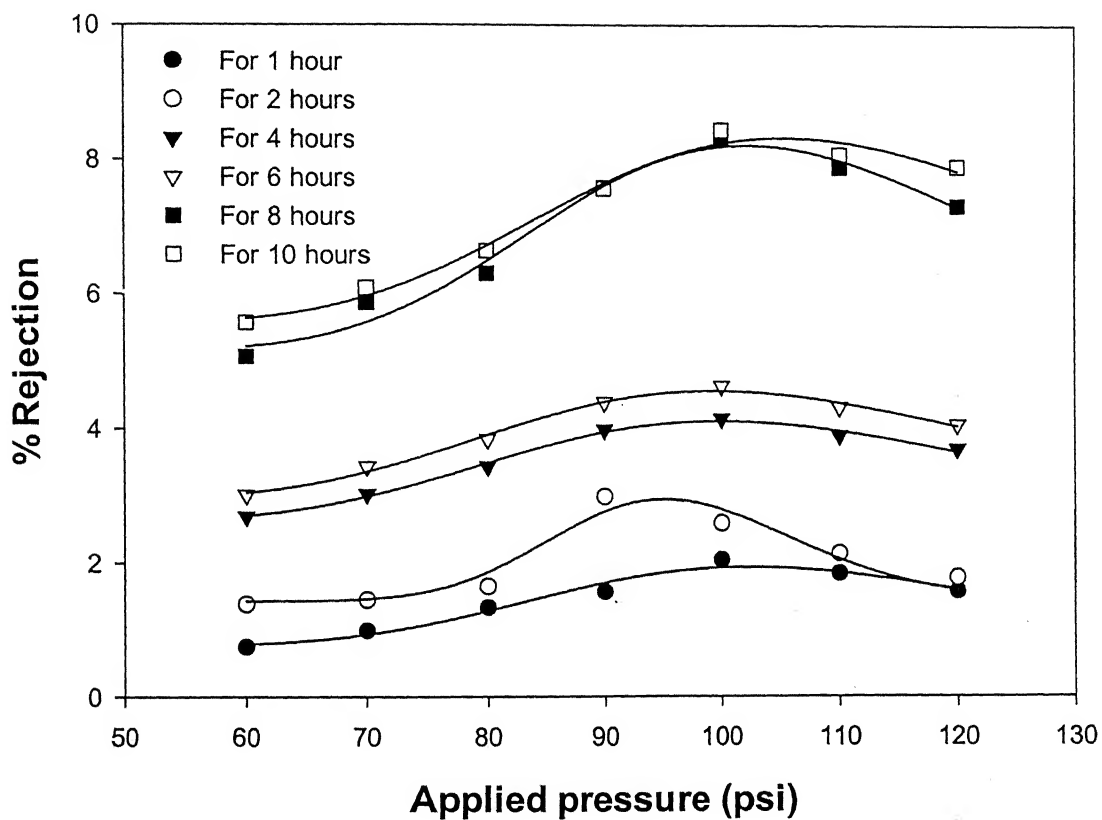
Figure-3.11.4, Rejection curves for $MgCl_2$ salt solution for different hours nitrated membrane.

Figure-3.11.5, Rejection curves for AlCl$_3$ salt solution for different hours nitrated membrane.

Figure-3.11.6, Rejection curves for $FeCl_3$ salt solution for different hours nitrated membranes.
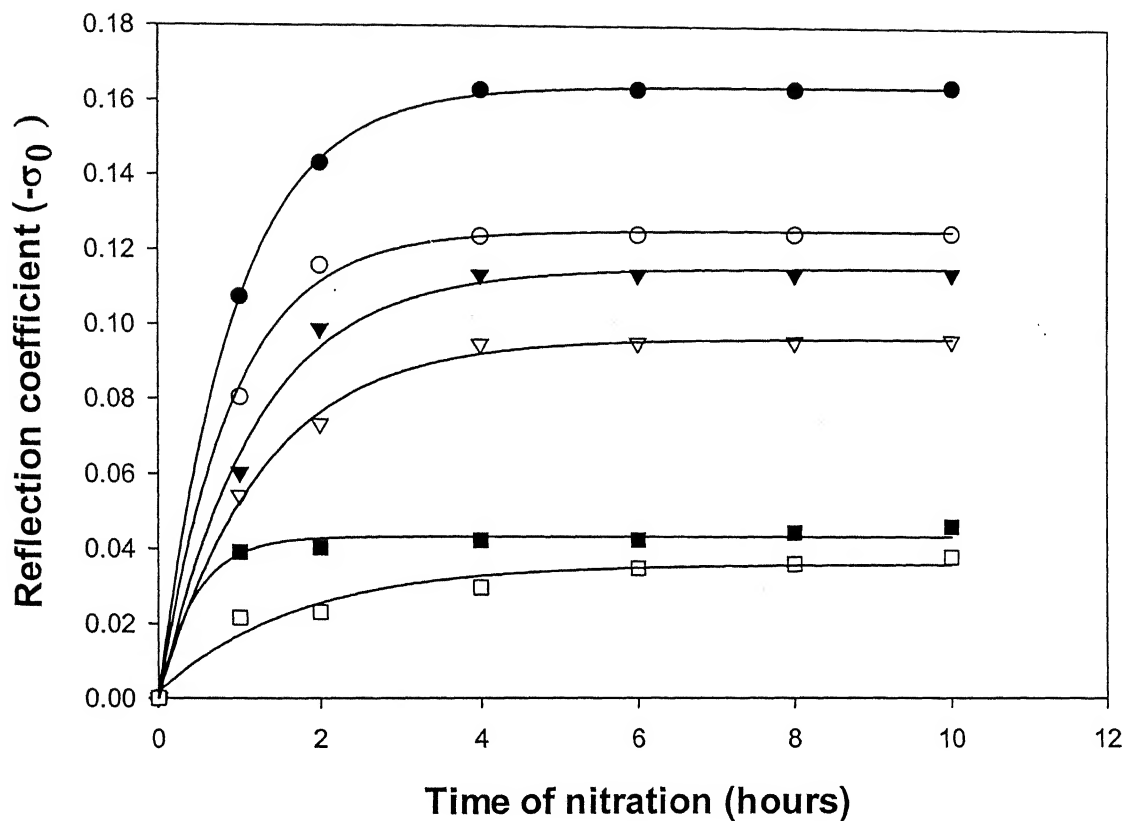
Figure-3.12.1, Plots of Reflection Coefficients Vs
Time of nitration.

● NaCl salt   ▼ CaCl$_2$ salt   ■ AlCl$_3$ salt

○ KCl salt   ▽ MgCl$_2$ salt   □ FeCl$_3$ salt
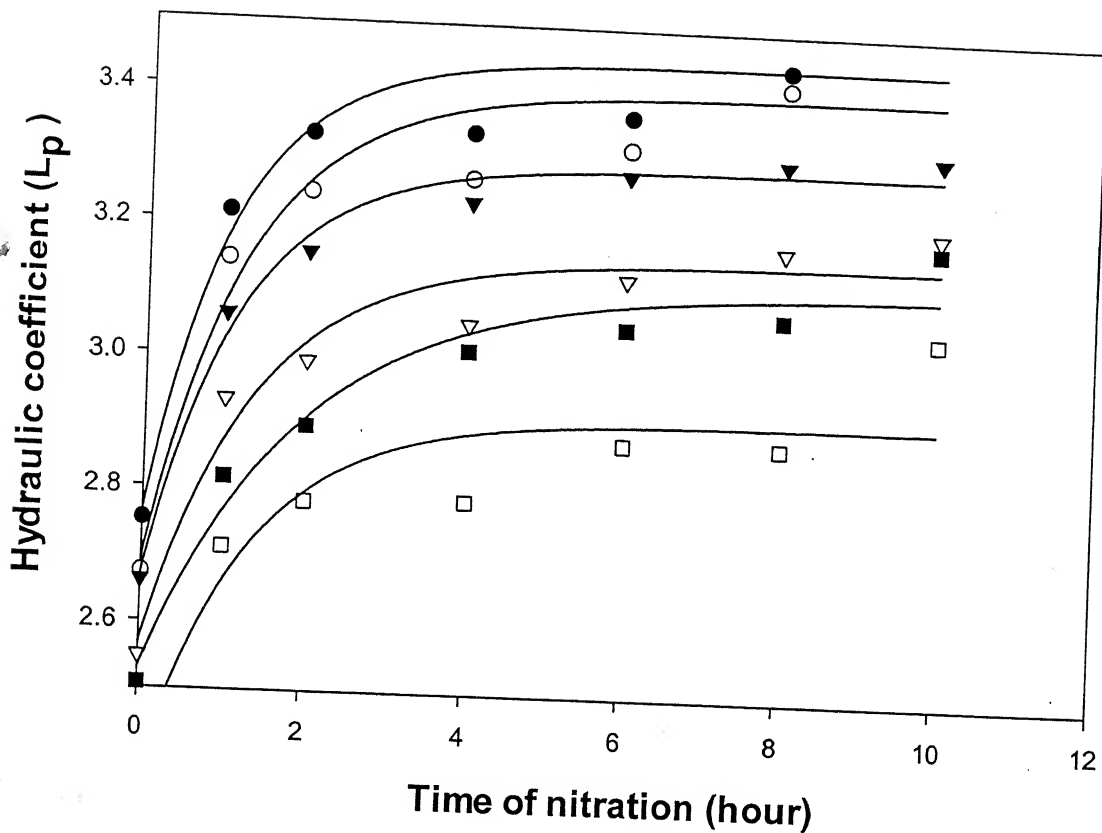
Figure- 3.12.2, Plots of Hydraulic Coefficient (L_p) Vs Time of nitration.

● NaCl salt   ▼ CaCl$_2$ salt
                                ■ AlCl$_3$ salt
○ KCl salt   ▽ MgCl$_2$ salt
                                □ FeCl$_3$ salt

Appendix-1
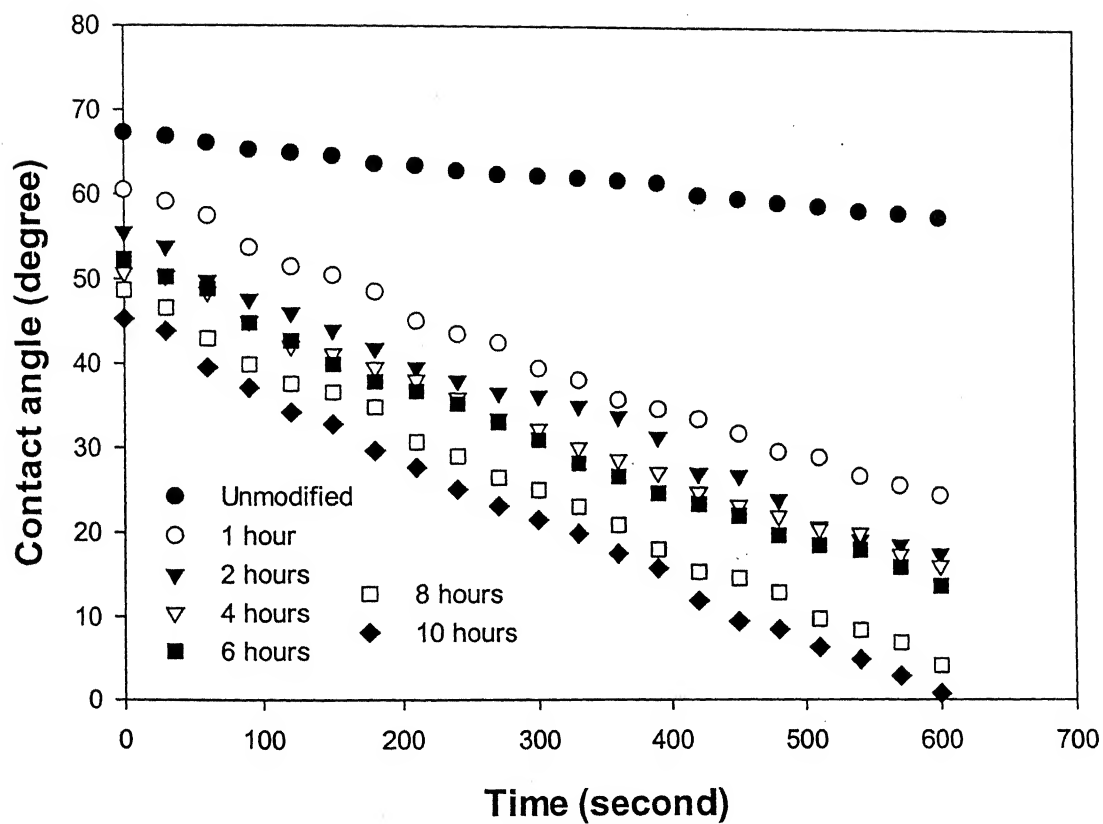
Plots of dynamic contact angle vs Time